USE OF N^{15}-TAGGED UREA-FORMALDEHYDE IN NITROGEN AVAILABILITY STUDIES

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ACKNOWLEDGMENTS

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INTRODUCTION

The pattern of uptake of soluble fertilizer nitrogen by crops
is characteristically inefficient, especially on sandy soils of Florida.
First, there is luxury consumption of nitrogen (subsequently designated
as N) soon after it is applied, followed by deficiency of N thereafter.
Second, soluble N is especially liable to loss from soil by leaching
or volatilization under adverse conditions.

Agronomists and agricultural chemists have sought to develop a
nitrogenous fertilizer material which would release N gradually over a
relatively long period of time at a rate sufficient to meet crop needs.
Ideally, it should be low in readily soluble N to minimize luxury con-
sumption and leaching. Natural organic sources often contain appreciable
amounts of rapidly available N. Several synthetic organic materials
have been developed and studied. Among the more promising are those
made by reacting urea and formaldehyde to give a condensation product
containing a significant amount of N in water-insoluble but slowly
available form.

Under certain conditions urea and formaldehyde react to form the
pure crystalline monomer methylenediurea. As conditions are varied,
methylenediureas polymerize irreversibly. Solubility and biological
availability of the N in the resulting polymers vary with conditions of
pH, reaction time, temperature and relative concentration of reactants.

Field, greenhouse and laboratory nitrification tests have demon-
strated that materials can be produced that have certain availability

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characteristics more desirable than those of mineral sources or natural organics. These tests have also shown that recovery of urea-formaldehyde N by crops is appreciably lower than from soluble inorganic sources. This poor recovery, coupled with the premium price paid for urea-formaldehyde fertilizers, introduces the question of their practicality as N fertilizer materials except for turf and ornamentals.

The purpose of this investigation was to quantitatively determine the destiny of N applied as urea-formaldehyde fertilizer. Materials were labeled with an abundance of the natural isotope N^{15}. Results are based on plant, soil and leachate recovery of labeled N. The portion of the applied N still unaccounted-for was assumed to have been lost in some form of gas to the atmosphere. Certain laboratory studies using closed systems were included to qualitatively determine, if possible, which volatile N compounds might be formed from these materials in the soil.

REVIEW OF LITERATURE

Urea-formaldehyde is a nitrogenous fertilizer material of fairly recent advent on the commercial market. The usual material contains around 38 per cent N, approximately two-thirds of which is insoluble in water (78). Interest in urea-formaldehyde condensation products as sources of fertilizer N developed in the early 1940's. Initial work was done by the Bureau of Plant Industry, Soils and Agricultural Engineering of the United States Department of Agriculture. Winsor (85) reports that Clark, Yee, Love, Arminger and Boyd did the primary work on these products and published on the subject during 1946-1951.

Yee and Love (88) state that the reaction of urea with formaldehyde forms a number of products depending upon the mole ratio of the reactants, reaction temperature, time and pH. A urea to formaldehyde ratio (U/F) of less than 1 and a pH of between 4 and 8 are used in the manufacture of plastics. When the mole ratio is increased above 1, products apparently contain methylene linkages between urea residues, and have terminal amino groups. Very high U/F ratios (7.5) produced pure crystalline methylenediurea. As the ratio was decreased the products became increasingly amorphous, less water-soluble and the surface area decreased, indicating formation of larger polymers. A series of urea-formaldehyde products were prepared by them with U/F reactant mole ratios ranging from 0.75 to 7.5. Products formed by these reactions had much narrower U/F ratios than the reactants, ranging from 0.88 to 2.0. Water solubility increased with an increase in U/F

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ratio. They assessed the availability of the N in these products by
determining their rate of nitrate production when incubated in a soil
at 30°C. Nitrification rates also increased with an increase in U/F
ratio. Products with U/F ratios ranging from 1.18 to 1.36 nitrified
at fairly constant rates for about three months and from then on at
reduced rates. Products with U/F ratios above and below this range
were not judged to be satisfactory as slowly available N sources.

Procedures using both dilute and concentrated solutions for re-
acting urea and formaldehyde are described by Clark et al. (25). Pro-
ducts differ in amounts of unreacted urea and relative proportions of
urea-formaldehyde complexes produced. With dilute preparations, pro-
ducts are lower in unreacted urea and in soluble materials because of
washing and of separation with the mother liquor.

Clark and co-workers (22,27) also reported that the reaction
between urea and formaldehyde appears to progress through methylolurea
to increasingly complex polymethyleneurea compounds. It has been shown
that the acid-catalyzed reactions produce a mixture of straight chain
compounds from methylenediurea to those containing more than six mole-
cules of urea (57).

Many other workers (21,22,25,26,27,59,82) report results of studies
conducted to evaluate the N availability patterns of urea-formaldehyde
reaction products, formed from a range of U/F reactant ratios. They
agree that while the commercial manufacture of high quality urea-
formaldehyde is complex and requires critical process control, products
can be made which approach ideal N availability characteristics.

These workers concur in their findings that water solubility and
N availability patterns of the products are largely determined by their

U/F ratios. They concluded that the products produced were mixtures of several compounds, probably ranging from small readily soluble methyleneurea molecules to long chain molecules, exhibiting differential solubility and breakdown in the soil.

Clark (21) states that the most promising urea-formaldehyde products contained 24 to 28 parts by weight of urea for each 10 parts of formaldehyde.

Clark and co-workers (25,26), in attempting to formulate a N solubility index for evaluating urea-formaldehyde condensation products, found that their solubilities in water increased with time and temperature. Therefore, a procedure was adopted whereby the amount of N dissolved from a 1 gram sample by 400 ml. of distilled water in 24 hours at 30°C. was established. Solubility index values obtained by this procedure were highly affected by U/F reactant ratios and correlated well with N availability patterns.

Fuller and Clark (36) conducted microbiological studies on urea-formaldehyde preparations. They report that hydrolytic enzymes of soil microflora are essential for liberation of ammonium-N, and that strict chemical hydrolysis of urea-formaldehyde is insignificant in the soil. Soil microflora activity was stimulated by urea-formaldehyde at rates far above practical importance in the field. This phenomenon was attributed to the carbon as well as N contained in urea-formaldehyde products.

Nitrification studies have been conducted on urea-formaldehyde products by many investigators (24,34,50,53,55,56,61.71,83,84). Rate of nitrate production was found to be affected by such factors as soil type, soil pH, temperature and characteristics of the compound being tested.

Winsor and Long (84) found that mineralization of N contained in urea-formaldehyde products increased with decreasing soil pH, with most rapid nitrification occurring in soils with initial pH of 5.5 to 6.0.

Long and Volk (53) reported that in all instances nitrification of the soluble portion of urea-formaldehyde products was enhanced by lime addition, and conversely the insoluble portion nitrified most rapidly without lime.

Clark and co-workers (27) devised a rapid laboratory method of evaluating urea-formaldehyde fertilizer materials as a refinement of the previously mentioned solubility index method (25,26). This procedure was based on the relative proportions of various compounds in urea-formaldehyde materials which were soluble in hot and cold water. An empirical value was obtained which correlated quite well with nitrification characteristics.

A modification of this procedure was published by Morgan and Kralovec (57). It was tested by the Association of Official Agricultural Chemists and accepted as the official activity index method for determining the fertilizer value of urea-formaldehyde products (30). The procedure involves determination of N insoluble in cold water (WIN), and of N insoluble in hot buffered phosphate solution (HWIN). Activity index (AI) of a material is the percentage of cold water insoluble N that dissolves in hot buffered solution.

$$AI = \frac{(WIN-HWIN) \times 100}{WIN}$$

This method is superior to other water solubility methods, and to the neutral permanganate method widely used for natural organics, as

an empirical means of indicating availability of N in urea-formaldehyde compounds (24,30). Clark et al. (24) state that the method shows close correlation with time consuming soil nitrification tests.

Slight modifications of the activity index procedure (28) have been tested and accepted by the Association of Official Agricultural Chemists (31) which make it applicable for assessing the quality of water-insoluble N contained in mixed fertilizers carrying urea-formaldehyde compounds.

A nitrification index procedure was described by Clark and co-workers (23,24,28). Nitrification index (N.I.) is defined as the per cent of added N not found as nitrate at the end of three weeks incubation but converted to nitrate in 15 weeks.

$$N.I. = \frac{100\ (N_{15} - N_3)}{100 - N_3}$$

Laboratory results (23) indicate a significant, but somewhat variable correlation between activity and nitrification indices. Minimum values (AI = 40, N.I. = 30) have arbitrarily been set as a basis for judging acceptability of the insoluble N portion of urea-formaldehyde compounds.

Disagreement exists as to the validity of empirical activity index measurements as indications of performance of urea-formaldehyde fertilizer products. Hayes (43) and Volk (78) state that activity index values are only approximate methods for controlling synthesis reactions and are not precise indications of quality or performance. On the other hand, Pereira and Smith (63) and Clark and associates (23,28) support the use of activity index values in determining agronomic usefulness of urea-formaldehyde fertilizers.

Arminger (7,8) evaluated 11 urea-formaldehyde preparations as sources of slowly available N for bermudagrass and perennial ryegrass. Results from the bermudagrass experiment showed that 69 and 97 per cent of the N supplied as Milorganite (an activated sewage sludge) and ammonium sulfate, respectively, were recovered the first 64 days. Urea-formaldehyde materials supplied only 32 and 57 per cent of the total N added during the same period.

Results from Arminger's perennial ryegrass experiment showed that a material supplying one-third of the N as a readily available source was inferior to a urea-formaldehyde material with 10 to 20 per cent readily soluble N. The latter produced better growth curves. Total yield of dry matter was slightly higher from urea-formaldehyde materials than from readily soluble sources, and availability patterns for urea-formaldehyde materials were far superior to Milorganite and urea.

Numerous other workers (1,14,39,40,46,54,58,59,72,86) have tested urea-formaldehyde materials on turfgrasses. There is general agreement that urea-formaldehyde materials can be used to replace or supplement N from other sources with little differential effect on turf quality. Application intervals may be extended up to five months, with success apparently dependent on development of adequate residual urea-formaldehyde N in soil (14). These workers state that the soluble portion nitrifies in three to four weeks and the insoluble portion at a rate of 6 to 7 per cent per month.

Volk et al. (79) reported a very poor showing of urea-formaldehyde fertilizer as compared to urea and ammonium nitrate topdressed on sandy soils growing oats and millet.

Scarsbrook (67) found urea-formaldehyde fertilizers to be less effective than ammonium nitrate for producing one-year crops of cotton

and corn. However, higher amounts of residual N were recovered from plots receiving the better grades of urea-formaldehyde materials than were recovered from plots receiving ammonium nitrate the previous year.

In general, it has been indicated that efficiency of nitrogen utilization is lower for urea-formaldehyde materials than for commonly used soluble materials (11,43,67,79). However, unreacted urea-formaldehyde materials are known to be residual in the soil after short-term plant uptake or nitrification studies. Therefore, Hayes (43) stated that observations must be made for at least 300 days and the whole plant must be analyzed to fairly demonstrate effectiveness of these materials. Observations have also been made that efficiency of recovery is predicated on development of a sufficient residue of slowly available urea-formaldehyde N in the soil (14,53).

No previous studies have been conducted to precisely account for all N added to a soil system as urea-formaldehyde, but numerous attempts have been made to construct soil N balance sheets for many other N fertilizer materials. The enigma of soil N balance sheets was extensively reviewed in 1954 by Allison (2).

The study of lysimeter data showed that an average of 15 per cent of the added N was not accounted-for in crops, soils and leachates, and that deficits were largely independent of the form of N added. Greenhouse data showed losses ranging from 0 to 50 per cent, and un-recovered N in field experiments ranged between 50 and 75 per cent. Unaccounted-for N was assumed to have been largely lost through leaching, but often gaseous losses were known to be considerable.

Laboratory studies conducted since Allison's review (4,12,16,17, 18,20,42,44,65,68,80) showed surprising agreement that recovery of N added to soil is virtually quantitative when soils are near neutrality and are supplied with optimum moisture and aeration. However, if conditions are varied from optimum, N recoveries are reduced. Losses are undoubtedly in the form of volatile compounds of N because all other forms can be measured with reasonable accuracy. Gaseous losses of N are discussed in detail in a subsequent part of this review.

Few lysimeter studies have been reported in the last decade. One conducted at Illinois by Owens (60) showed an average loss of 33 per cent of added N, presumably by bacterial denitrification.

Results of a 20-year lysimeter experiment were reported by Pratt et al. (64). They concluded that there was no evidence of non-symbiotic N fixation or volatile losses of N. However, it seems improbable that the effects of these two phenomena could be determined in a non-replicated experiment with untagged N.

Two lysimeter studies on Lakeland sands are of importance. Volk (77), using unlabeled N, recovered 50 to 80 per cent of applied N in crops and leachates, depending on application rate and conditions. Allison and co-workers (5) found no evidence of gaseous losses of N except where animal manure was applied with sodium nitrate.

A review of several greenhouse experiments published since 1955 (41,47,52,74,81) showed recoveries of added N, including that residual in soil, ranging from 70 to 97 per cent and averaging 86 per cent. In most cases authors felt that the incomplete recoveries of applied N were due to denitrification. Jansson (47) reported that losses occurred only while N added to soil was in inorganic form. Losses were slightly higher with sodium nitrate than with ammonium sulfate.

Loewenstein et al. (52) reported similar recoveries from nitrate and ammonium sources. However, losses of N from uncropped soils ranged from 35 to 72 per cent while similarly treated cropped soils lost only 7 to 8 per cent of the applied N.

N recovery data from field experiments do not account for leaching losses and rarely include soil analyses. Usually only the N recovered in the crop is measured. This is obtained by subtracting appropriate values for control plots from the values for fertilized plots. Any gain or loss of soil N is unknown and validity of this calculation assumes equal input of N from seed, rain, fixation and soil changes.

Viets (76) used such methods to calculate recoveries of fertilizer N on irrigated soils in western United States. He reported recoveries of 9 to 50 per cent of applied N for fine textured soils and an average of about 80 per cent for sandy soils.

Pearson et al. (62) applied five sources of N to field plots in the southeast. Fall-applied N was about 62 per cent as efficient as spring-applied N, indicating leaching or other losses. Recoveries of spring-applied N ranged from 50 to 59 per cent in the first crop, and two succeeding unfertilized crops recovered 18 to 30 per cent, making total recoveries of 70 to 77 per cent of the applied N in three crops.

Labeled N has been used in a few cases to test efficiency of N recovery in the field. One such experiment reported by Carter and co-workers (19) was conducted in cylinders driven into field soil to depths of 18 to 24 inches. Tagged sodium nitrate and ammonium sulfate were added at a rate of 250 pounds of N per acre. Some cylinders were cropped with sudangrass and others left uncropped. N recovered in the soils and plants of 32 cylinders ranged from 85 to 93 per cent and averaged 89.5 per cent of that applied.

Both tagged and untagged methods of determining N recovery are
widely used. Comparable results appear to be obtained if whole plant,
leachate and soil N are determined when using labeled N, or when
leaching is prevented and subsequent crops are grown to remove residual
N in the non-tracer method.

The addition of fertilizer N is known to increase uptake of non-
fertilizer soil N by plants (51,81). Walker and co-workers (81) attri-
buted incorporation of labeled N into the soil N complex to two processes.
The first was ordinary interchange between labeled N and soil N. The
second was a tieup of added tracer N by soil organisms whose activity
was stimulated by increased root excretions. Legg and Allison (51)
placed most emphasis on the latter explanation.

The preceding discussion has indicated that losses of applied N
are through two major channels: leaching and volatilization. Leaching
losses are the more tangible and often the most apparent of the two.

Volk (77) found only slight leaching of N through 50-inch
lysimeters filled with Lakeland fine sand growing various pasture grasses.
The author stated that while leaching losses were appreciable at least
one of three years the test was conducted, the low recovery of N by
grasses cannot be attributed primarily to leaching losses.

Tyler et al. (75) traced the movement of ammonium-, nitrate-
and urea-N in simulated cross sections of field soils. They reported
little downward movement of ammonium-N except in sandy soils. Upward
movement of ammonium-N occurred to some extent while nitrate-N moved
freely with the wetting front.

It is believed that while nitrate-N is very mobile, there is an
appreciable resistance to its leaching beyond the root system of vigor-
ously growing grass (77).

A few organic substances, such as methylamine, trimethylamine, hydrocyanic acid and nicotine may be exuded from plants and lost by volatilization (2). These losses are believed to be negligible, with most of the N being returned to the soil.

Volatile losses of N, other than ammonia, occur primarily through biological denitrification and to a lesser extent from chemical decomposition of nitrite (2). Nitrous oxide and molecular nitrogen gas are the primary products of denitrification (4,12,15,16,17,29,42) while nitric oxide is formed by the chemical decomposition of nitrites (18, 20,37,80,87). Nitric oxide is subject to reabsorption by the soil and subsequent conversion to nitrates, or possible loss as nitrous oxide or nitrogen gas (69).

Two recent papers described the sequence of products formed during denitrification. Cady and Bartholomew (15), using mass spectrometer techniques, and Cooper and Smith (29), using gas chromatography, found the sequence of products formed in denitrification proceeded from nitrate to nitrite to nitrous oxide and finally quantitatively to nitrogen gas. Occasionally small amounts of nitric oxide were noted, but they were rapidly converted to other forms of N. Other pathways and intermediates may function in denitrifying systems but could not be determined in these studies. Denitrification is enhanced by excess water or carbon dioxide which causes a restricted supply of oxygen; and by an abundance of readily decomposible organic matter.

Volatile losses of N during the aerobic oxidation of ammonium-containing or producing compounds is generally agreed to be through decomposition of excessive accumulations of nitrites. Nitrites may accumulate in a soil that is too acid for complete biological oxidation

to nitrate (18) and decompose with resulting losses. Nitrites also accumulate when large amounts of urea or ammonium-N are added to a soil resulting in a high pH. Ammonia inhibits nitrate production much more than nitrite production under alkaline conditions (13,22,37). As the ammonium is oxidized and decreases in concentration, the pH of poorly buffered soils lowers and loss of N from breakdown of nitrites results.

Wullenstein et al. (87) reported evidence that the breakdown of nitrites in soil may be an oxidation-reduction mechanism where exchangeable heavy ions reduce nitrate to nitric oxide. Other mechanisms for volatile losses of N have been postulated, but are considered to be of minor importance (3).

The remaining portion of this review discusses the literature specific to the use of the natural isotope of N (N^{15}) in soil N studies.

In the past, field, greenhouse and lysimeter studies alike have suffered from several basic limitations. Among these were inability to determine non-symbiotic N fixation, inability to determine small changes in soil N content and inability to accurately differentiate between N supplied to a plant by soil or fertilizer. The advent of the use of isotopic N has offered a means of surmounting these limitations.

Enrichments of N^{15} have been efficiently employed in more soil and plant N studies than is feasible to note here. Only a few of the publications most pertinent to the actual design and analysis of this study are included in this review.

In planning an experiment using N^{15} an estimation must be made regarding the concentration and amount of tracer N to place in the experimental system. Too low an amount of N^{15} introduces the possibility that errors in analysis may approach the magnitude of differences among

treatments (9,70). Too high an amount (quantity and/or isotopic concentration) wastes the expensive material.

Two factors combine to determine the quantity of N^{15} required in a particular experiment. The first is the dilution effect of soil N with added isotopic N. Second, the analytical error in determining total and tracer N must be considered.

Knowledge of total N in the soil to be used as well as results from previous tracer experiments (10,45,47,51,60,68,73,74,81) are practical guides in estimating natural dilution of soil N. Extent of isotopic dilution is dependent upon the quantity of N which occurs in the experimental system in a form which mixes with the tracer, in relation to the amount of tracer supplied (9,45). If recovery data is obtained by analyzing total soil N, the entire amount of soil N must be considered, but if recovery is based on cropping and solution extraction, only the quantity of N in the available pool need be considered (45,48). Smith et al. (70) stated that an enrichment of 5 per cent excess N^{15} or less should be adequate for short-term plant uptake experiments where only the plant material is to be analyzed. Enrichments of 10 to 20 per cent excess N^{15} is recommended for long-term plant uptake experiments where residual soil N is also measured. In any case, sufficient enrichment of N^{15} must remain in all N fractions analyzed at termination of experiment so that experimental errors are low in relation to amounts of tracer N measured (9,10).

The use of tracer N may reduce, but does not eliminate, sources of error which are inherent to total N determinations. According to Bartholomew (9), these sources of error are site variation, subsample variations and errors in measurement of individual samples. Bartholomew

and co-workers (10) concluded that changes in experimental design which might reduce experimental error are: 1) increased replication; 2) increased sample size; 3) increased concentration of N^{15} in fertilizer materials.

Several basic assumptions are employed in the analysis of tracer data. The first is that biochemical and non-biological reactions do not discriminate between the isotopes of N. This assumption is not strictly valid but errors introduced through this assumption are believed to be insignificant in comparison to sampling and experimental errors (9).

A second assumption is that the isotopes of N combine and react in a purely random manner in all biological, chemical and physical reactions taking place throughout the duration and analysis of the experiment. The calculations of mass spectrometer data are based upon this assumption accoring to Rittenberg (66). The slight errors which may exist in its validity, like those associated with the first assumption, do not introduce significant errors in most experiments.

Mathematical equations for estimating N transformations in soil have been advanced by Kirkham and Bartholomew (48). Such equations have been useful in estimating N mineralization and immobilization in soil systems (45). However, subsequent indications (47,51,74) that some of the basic suppositions upon which these equations are based may not be valid. Tyler and Broadbent (74) conclude that plant uptake of tracer N may not provide an accurate measure of fertilizer efficiency because of isotopic dilution of N^{15} enriched fertilizer N with soil N. However, the whole question of available N is tied up in the process of biological exchange, both in the presence and absence of fertilizer N. These authors believe biological side-reactions actually provide the key to understanding of N fertility in soils.

The N^{15} content of N materials is determined by converting all N to ammonia by common Kjeldahl procedure and determining total N in the usual way. The ammonia is reacted with alkaline sodium hyprobromite to liberate N_2 gas. The final step is carried out under vacuum to eliminate contamination from atmospheric gasses. Proportions of N^{14} and N^{15} isotopes contained in the N_2 gas are determined with a mass spectrometer. Several methods have been published for carrying out these operations (38,66,70).

In summary, the literature indicates that certain urea-formaldehyde products are good sources of slowly available N, but in many cases the efficiency of N utilization by plants has been comparatively low. Urea-formaldehyde N not taken up by initial cropping appears to be residual in the soil and at least partially available to subsequent crops.

Efficiency of N utilization and pathways of loss have been extensively studied for many fertilizer materials and many crops under a wide range of conditions. Leaching of nitrates, biological denitrification and various chemical reactions producing volatile products of N are believed to be major pathways of N loss from soils. Chemical trapping, gas chromatographic, infra-red and mass spectrometric methods have been successfully used in studying volatile losses of N.

Experimental methods utilizing the natural isotope of N (N^{15}) have been widely used and are well adapted to studying plant utilization of fertilizer N. If care is taken in designing experiments with N^{15}, and the investigator familiarizes himself with the basic assumptions involved in obtaining and interpreting tracer N data, much valuable information will result from this technique.

METHODS AND MATERIALS

This study was conducted from October, 1962, to May, 1964. It was carried out in three phases: 1) an outdoor lysimeter; 2) a greenhouse; 3) a laboratory phase. Primary N recovery data were obtained from lysimeter and greenhouse phases. The laboratory incubation phase was conducted as a supplementary part of this investigation, as time allowed and prior results indicated. Its purpose was to determine the nature of volatile N products which might be produced from N applied to soils as ammonium nitrate and urea-formaldehyde, and to indicate conditions conducive to such losses.

Lysimeter Phase

The physical set-up consisted of 12 buried outdoor lysimeters made from 12-inch (diameter) glazed tile, 36 inches long. Surface soil area was 113 square inches or 1.80×10^{-5} acre. The bottom of each lysimeter was sealed with an inverted cone of concrete lined with a plastic sheet and sealed on the outside with asphalt varnish.

The cone was filled with fine gravel and washed sand, and then covered with a thin layer of glass wool. A one-fourth inch (outside diameter) plastic tube tapped the bottom of the cone and extended through the center of the lysimeter to 6 inches above the soil surface. Leachates were removed through this tube with a suction pump.

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A removable plastic-covered hood was constructed and placed over the lysimeters to protect the grass when cold temperatures occurred in the winter.

The soil used was Arrodondo fine sand grading toward Fort Meade fine sand. Soil was placed in lysimeters in three profile horizon layers: 0 to 6 inches; 6 to 12 inches and 12 to 36 inches. Surface soil description is presented in Table 1. Dolomite was incorporated at a rate of 2,000 pounds per acre in the surface 6 inches. Coastal bermudagrass was sprigged into the soil on November 2, 1962, to serve as the test crop.

Table 1--Composition of lysimeter soil.

Soil characteristic	Value
Texture	Fine sand
pH, 1:1-soil:water	5.4
Organic carbon	0.31%
Total N	0.033%
Exchangeable CaO*	336 lbs. per acre
Exchangeable MgO*	65 lbs. per acre
Soluble P_2O_5*	30 lbs. per acre
Soluble K_2O*	83 lbs. per acre

*Ammonium acetate (pH 4.8) extraction.

Major fertilizer nutrients were applied to the lysimeters at rates equivalent to 25 pounds N, 100 pounds P_2O_5 and 100 pounds K_2O per acre on

November 2, 1962. Amounts of P_2O_5 and K_2O equivalent to 100 pounds per acre each were subsequently applied on April 22, 1963. Ferro Corporation F.T.E.-501 minor element frit was applied at a rate equivalent to 20 pounds per acre to all lysimeters on the latter date.

Measurements were made on rainfall and soil temperature (4-inch depth) at the experimental site throughout the experiment. Supplemental unrecorded amounts of irrigation water were added frequently.

A completely randomized experimental design with three replications was employed. Treatments consisted of the following N applications:

1) NH_4NO_3, 150 pounds N per acre at 9.091 atom per cent excess N^{15} of NH_4^+-N (42.80 meq. NH_4^+-N per lysimeter).

2) NH_4NO_3, 150 pounds N per acre at 8.973 atom per cent excess N^{15} of NO_3^--N (42.12 meq. NO_3^--N per lysimeter).

3) Urea-formaldehyde, 150 pounds N per acre at 9.907 atom per cent excess N^{15} (85.75 meq. N per lysimeter).

4) Urea-formaldehyde, 300 pounds N per acre at 9.907 atom per cent excess N^{15} (171.50 meq. N per lysimeter).

All tagged NH_4NO_3 materials were made from a solution of 50 per cent HNO_3 with 19.5 per cent N^{15} enrichment, supplied by Spencer Chemical Company. $NH_4N^{15}O_3$ was made by adding NH_4OH to appropriately diluted tagged HNO_3, to the methyl red endpoint. $N^{15}H_4NO_3$ was formulated by reducing tagged HNO_3 using a soda-zinc method (6) and distilling NH_3 into a calculated excess of unlabeled HNO_3. The excess acid was then titrated to the methyl red endpoint with NH_4OH.

The labeled urea-formaldehyde material was supplied by Allied Chemical Company. This material contained 37.87 per cent total N, with 9.907 atom per cent excess N^{15}. Particle size was somewhat finer

than commercial urea-formaldehyde. All of it passed a 10 mesh screen.
It had an activity index of 60 and contained 4.61 per cent urea N,
10.2 per cent non-urea water-soluble N, and 24.0 per cent cold-water-
insoluble N. After application, each fertilizer material was carefully
analyzed for total N content and N^{15}/N^{14} ratio. Sample preparation and
measurement of isotope ratios of N used in this study are described by
Smith et al. (70).

Nitrogen treatments were applied to well established coastal
bermudagrass on December 13, 1962. Applications were made by removing
soil plugs, mixing ammendments with the removed soil and replacing in the
original hole. Seven plugs 2 inches in diameter and 6 inches deep were
extracted from each lysimeter. This allowed treatments to be concen-
trated in 19.5 per cent of the surface 6-inch layer of soil.

Leachates were collected periodically, acidified, concentrated
by evaporation and analyzed by a modified Devarda's alloy method (6)
for soluble N content.

Plant tops were harvested periodically, dried at 65°C., weighed
and analyzed for total N by a modified Kjeldahl-Gunning method (6).
Plant harvests were composited into three groups: 1) December 13, to
March 31; 2) April 1, to July 17; 3) July 18, to December 12. Each
of the three groups was analyzed for N^{15}/N^{14} isotope ratio. Grass
roots were analyzed in a similar manner at termination of the study.

Soils were sampled at termination of the study in the following
manner:

1) One and one-half inch diameter plugs, 5 inches deep from
   center of treated 2-inch cores.

2) One-half inch diameter plugs, 7 inches deep from between

treated 2-inch cores.

3) Total soil from 7 to 12-inch zone.

4) Total soil from 12 to 36-inch zone.

Soil from each zone was weighed, sampled for moisture content,
air dried and ground to an impalpable powder in a hammer mill. Soluble
plus exchangeable N was determined in soils from zones 1) and 2) above
in the following manner. Forty grams of soil were placed in 500 ml.
Erlenmeyer flasks and shaken with 400 ml. of 2N KCL for one hour. The
suspensions were filtered through Whatman No. 1 filter paper, and 350 ml.
of the clear filtrate measured into 800 ml. Kjeldahl flasks. Two grams
of Devarda's alloy metal powder and 4 grams of carbonate-free MgO were
added to the flasks. They were placed on a distillation apparatus,
connected to H_3BO_3 collection flasks and allowed to stand for several
minutes without heat until reaction had subsided. Heat was then
gradually applied until 200 ml. of distillate were collected. N content
was determined by titration with standard 0.1N H_2SO_4 to the purple
endpoint of a methyl red-methylene blue mixed indicator.

Total N was determined on 15 gram samples from all four soil zones
by the Kjeldahl-Gunning method modified to include nitrates (6). Iso-
topic ratio of N^{15}/N^{14} was determined on total N from the first three
soil sampling zones.

Greenhouse Phase

A randomized block design with three replications was used in
this study. Leon fine sand at pH values of 5.6 and 6.3 and Ona fine

sand at pH 5.3 comprised the three blocks. Four N treatments were
randomly applied to the soils in each block. The treatments were as
follows:

1) No N added.

2) NH_4NO_3, 150 pounds N per acre at 16.73 atom per cent
   excess N^{15} of NH_4^+-N (19.74 meq. NH_4^+-N per pot).

3) NH_4NO_3, 150 pounds N per acre at 17.17 atom per cent
   excess N^{15} of NO_3^--N (19.93 meq. NO_3^--N per pot).

4) Urea-formaldehyde, 300 pounds N per acre at 9.907 atom
   per cent excess N^{15} (81.69 meq. N per pot).

Glazed porcelain 2-gallon pots were filled with 9600 grams of
soil taken from the surface 6 inches of the three soil type areas. N
applications were made by removing the surface 4 inches of soil from
each pot, incorporating ammendments into the removed soil and replacing
in the original pot. N treatments were applied, coastal bermudagrass
was sprigged, and equivalents of 90 pounds per acre of P_2O_5 and 100
pounds per acre of K_2O were applied on January 15, 1963. The same
application of P_2O_5 and K_2O were subsequently repeated on April 17, 1963.

Duration of this study was approximately eight months, running
from January 15, to September 12, 1963. The bermudagrass was cut
periodically until August 1, when all bermudagrass tops and roots were
harvested. Pots were replanted to millet, and harvested once at termin-
ation of the study.

Bermudagrass and millet tops, roots and soil samples were analyzed
for total N. Composite samples of all grass clippings, as well as roots
and soils, were analyzed for isotopic ratio of N^{15}/N^{14}.

Water was applied in a manner which supplied crop needs but caused no leaching.

Laboratory Phase

Three incubation studies were conducted. The first was under aerobic conditions, and the second and third in anerobic systems. The soil used in all cases was similar to the 0 to 6-inch horizon of lysimeter soil.

Experiment Number 1

This experiment was set up using the same randomized design and the same treatments as the lysimeter study. Five hundred grams of soil were placed in each of twelve 500 ml. wide-mouthed Erlenmeyer flasks. To the soil in each incubation flask was incorporated 500 mg. dolomite, 47 mg. K_2HPO_4 and 5 grams of sucrose. Moisture levels were held at 12 per cent of oven-dry soil weight, slightly below field capacity.

Incubation flasks were closed with a 2-hole stopper fitted with glass tubing to permit a constant stream of air to pass over the soil. Air was supplied from compressed air lines in the laboratory. It passed through scrubbers of $\underline{N}$ H_2SO_4, $\underline{N}$ NaOH and water, to trap NH_3, CO_2 and acid oxides of N (NO, NO_2) and to humidify the air, respectively. After passing through the incubation flasks, air was bubbled through test tubes containing H_3BO_3 and KOH to trap evolved NH_3 and acid oxides of N, respectively. Quantitative CO_2 evolution measurements were not made.

In an aerobic atmosphere NO oxidizes spontaneously:

$$2NO \ + \ O_2 \longrightarrow 2NO_2 \xrightarrow{\text{H}_2\text{O}} HNO_3 \ + \ HNO_2$$
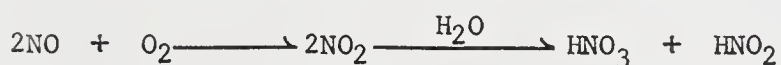
Qualitative tests for evolved oxides of N were made by testing for the presence of nitrate in the KOH solution by the diphenolamine test (6).

Duration of this test was 80 days at ambient room temperature and an air flow rate of approximately 100 ml. per minute.

Experiment Number 2

Incubation vessels used in this experiment were 500 ml. vacuum flasks fitted with glass stopcocks on the vacuum arm. Number 7 rubber stoppers, each bored and fitted with a glass tubing 9 mm. in diameter, 1-inch long, and capped with a large rubber serum cap, were used to seal the tops of the flasks. The serum caps and stopcocks were coated heavily with a commercial vacuum grease to eliminate air leaks.

Five hundred grams of soil, ammended with 500 mg. dolomite, 47 mg. K_2HPO_4, 5 grams sucrose and 60 ml. of water, was placed in each flask.

The following treatments were incorporated into the soil of the flasks:

1) No N added.

2) NH_4NO_3, 75 mg. N.

3) Urea-formaldehyde, 75 mg. N.

4) Urea, 75 mg. N.

The experiment was set up in a completely randomized design with two replications.

After treatments were applied, the atmospheres of the incubation flasks were repeatedly evacuated with a vacuum pump and flushed with helium (He) gas. When virtually all oxygen (O_2) and N (N_2) gasses had been removed, a 100 per cent He atmosphere was left in the flasks. Pressure within the flasks was kept slightly above atmospheric pressure to reduce the tendency for air to contaminate flask atmospheres.

The flasks were incubated at ambient room temperature (between 25° and 29°C.) for the 7-day duration of this test.

Incubation flask atmospheres were sampled and analyzed daily for content of O_2, N_2, NO and N_2O. Sampling procedure was as follows: 1 ml. of water (boiled to remove dissolved gases) was placed in a 2.5 ml. syringe, made air-tight by coating the plunger with vacuum grease. Air was removed from the syringe and the water was injected into the flask through the rubber serum cap. One ml. of flask atmosphere was drawn into the syringe. The needle was withdrawn from the serum cap and immediately inserted into a rubber stopper to await injection into the gas chromatograph.

Analysis was carried out on a Perkin Elmer Model 154L gas chromatograph, with a thermister detector system, connected to a Sargent Model SR recorder. Helium was used as the carrier gas at a flow rate of 50 ml. per minute. A dual column arrangement was used with a Linde Molecular Seive-5A column separating O_2, N_2 and NO, but irreversibly adsorbing N_2O. A silica gel column with an ascarite section on the anterior end separated N_2O from other air components. CO_2, which was not separated from N_2O by the silica gel column, was removed by the ascarite section.

Columns were mounted on 2-way stopcocks which permitted use of one column at a time. Column materials were 30 to 60 mesh size. They were packed in glass columns with 3.5 mm. inside diameter and 6.0 mm. outside diameter. The molecular seive column was 38 inches long and the silica gel column 12 inches long, the latter preceded by a 12-inch section of ascarite.

Experiment Number 3

This test was carried out in identical manner except that different N treatments were used. It was incubated in an oven at 30°C.

Treatments used in this test were:

1) No N added.

2) Uramite, 75 mg. N.

3) Washed Uramite, 75 mg. N.

4) Methylenediurea, 75 mg. N.

5) Hydroxylamine, 75 mg. N.

6) Urea, 75 mg. N.

Sampling procedures and analyses were the same as described for Experiment Number 2 except that flask atmospheres were not analyzed for N_2O in this study.

RESULTS AND DISCUSSION

The summarized data on dry matter yields and N uptake are pre-
sented in tabular and graphic form. All values are averages of three
replications, except in the laboratory gas analysis phase where only two
replications were used.

Results of the outdoor lysimeter, greenhouse and laboratory phases
of this study are presented separately. Primary emphasis has been
placed on results of the outdoor lysimeter study, because this phase
most closely approximated true field conditions. Results of the green-
house phase are discussed only as they corroborate, provide additional
information or otherwise affect the discussion of results of the
lysimeter phase.

Results of the laboratory phase are presented in tabular form.
They are discussed primarily for the purpose of suggesting reasons for
some of the unaccounted-for N in the lysimeter and greenhouse balance
sheets.

Lysimeter Phase

Monthly rainfall data for the 12 months of this study are pre-
sented in Table 2. The amount of water which passed through the profiles
of the lysimeters and was collected as leachates each month is also
presented in this table. Rainfall data are of limited value, since sub-
stantial amounts of supplemental water were added throughout the year

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Table 2--Monthly rainfall and leachate for the 12 months duration of
the lysimeter study.

Date	Inches rainfall	Inches leachate[a]
December, 1962[b]	0.64	--
January, 1963	2.21	--
February, 1963	4.52	0.4
March, 1963	2.56	0.3
April, 1963	· 1.30	0.3
May, 1963	3.51	1.0
June, 1963	3.57	0.8
July, 1963	6.83	1.5
August, 1963	3.21	0.9
September, 1963	3.14	0.8
October, 1963	0.26	1.1
November, 1963	3.25	1.4
December, 1963[c]	1.36	1.9

[a]Average per lysimeter.

[b]December 13, to 31, 1962, only.

[c]December 1, to 12, 1963, only.

to keep the grass from wilting. At no time was an excess of irrigation water added which might contribute to significant leaching.

No measurable amounts of N were found in leachates of any of the lysimeters for the first six months of the experiment. Grass was well established and growing vigorously during this time. Apparently it was very efficient in retaining nitrates within the root zone. No rapid movement of water through the soil profile occurred during the first six months. This resulted in no accumulation and movement of nitrates from the root zone with the wetting front.

Appreciably more water passed through the lysimeters in the last six months than in the first six months of the study. Nevertheless, only very small amounts of N were detected in the leachates. Amounts ranged from less than 1, up to 5 meq. of N for any given lysimeter. Samples containing the highest amounts of N were checked for content of N^{15} with the mass spectrometer. None of the leachates was found to contain N with a content of N^{15} significantly above normal abundance (0.375 per cent). For this reason, the amounts of applied N leached from the soil were assumed to be insignificant under conditions of this test.

The possibility exists that N was leached from the lysimeter soils but was volatilized and lost by denitrification or chemical reaction in the storage bottles. However, small amounts of copper sulfate and about 0.1 per cent toluene were added to stored leachates to eliminate microbial activity, and they were kept out of direct sunlight to reduce photo-chemical reactions. It is assumed that errors in total N recovery introduced by any denitrification during storage was negligible when compared to sampling and analysis variations for the soils.

Soil temperatures (4-inch depth) ranged from a minimum 8:00 A.M. temperature of 36°F. to a maximum 5:00 P.M. temperature of 70°F. through the winter months. Soil temperatures ranged from 65°F. to 90°F. during the warmer months.

In the subsequent discussion of treatment effects the 150 pounds N per acre rate is referred to as the standard application and the 300-pound application as the double rate.

Dry matter yields of coastal bermudagrass were significantly affected by source of N and by rate of urea-formaldehyde application (Table 3 and Figure 1). Ammonium nitrate produced significantly higher yields of dry matter than the same N application from urea-formaldehyde only on the 108-day harvest. Comparable yields were obtained for all other harvest dates. This single harvest caused the cumulative yields of dry matter obtained from urea-formaldehyde to be lower than those from an equivalent rate of ammonium nitrate N, at the end of the study. The differential response of coastal bermudagrass to equivalent rates of N, applied as ammonium nitrate and urea-formaldehyde, occurred entirely during the 52- to 108-day interval.

The double rate of urea-formaldehyde produced significantly higher yields of dry matter than did the standard rate of ammonium nitrate on the 189-, 216- and 278-day harvest dates, and for the total period. The double rate produced significantly more dry matter than the standard rate of urea-formaldehyde on the 108-, 189- and 216-day harvest dates, and for the total period.

Total N taken up by coastal bermudagrass from the various N treatments (Table 4 and Figure 2) shows the same general trends as dry

Table 3--Yields of coastal bermudagrass tops from lysimeters.

N treatment		Dry matter yield in grams per lysimeter							
Source	Meq. per lysimeter[a]	Harvest data (days after fertilization)							
		47	51	108	189	216	278	363	Total
$N*H_4NO_3$	85.6[a]	5.0	12.6	21.0	25.1	9.6	13.8	27.5	114.6
	85.6[a]	3.5	6.7	28.8	25.2	10.5	12.3	41.8	128.8
	85.6[a]	3.2	9.6	27.6	28.7	7.7	11.1	33.0	120.9
Average yield		3.9	9.6	25.8	26.3	9.3	12.4	34.1	121.4
NH_4N*O_3	84.2[a]	1.4	16.9	21.9	30.2	10.2	13.4	27.7	121.7
	84.2[a]	1.6	8.3	25.4	22.6	10.9	11.5	39.9	120.2
	84.2[a]	2.3	9.1	25.4	25.7	9.6	11.3	33.9	117.3
Average yield		1.8	11.4	24.3	26.2	10.2	12.1	33.8	119.8
U-F*	85.7[a]	3.4	9.4	14.0	25.0	9.1	16.6	40.2	117.7
	85.7[a]	1.7	10.1	13.2	30.8	11.1	13.2	32.4	112.5
	85.7[a]	3.7	6.5	9.3	23.2	9.7	12.2	25.2	89.8
Average yield		2.9	8.7	12.2	26.3	10.0	14.0	32.6	106.7
U-F*	171.5[b]	4.4	9.8	22.7	34.6	16.3	17.1	25.9	130.8
	171.5[b]	3.7	9.8	24.4	36.6	18.9	18.6	39.8	151.8
	171.5[b]	2.6	8.8	26.9	55.6	16.6	16.2	36.5	163.2
Average yield		3.6	9.5	24.6	42.3	17.3	17.3	34.1	148.7

Coefficient of variation for total yields is 11.9 per cent.

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.
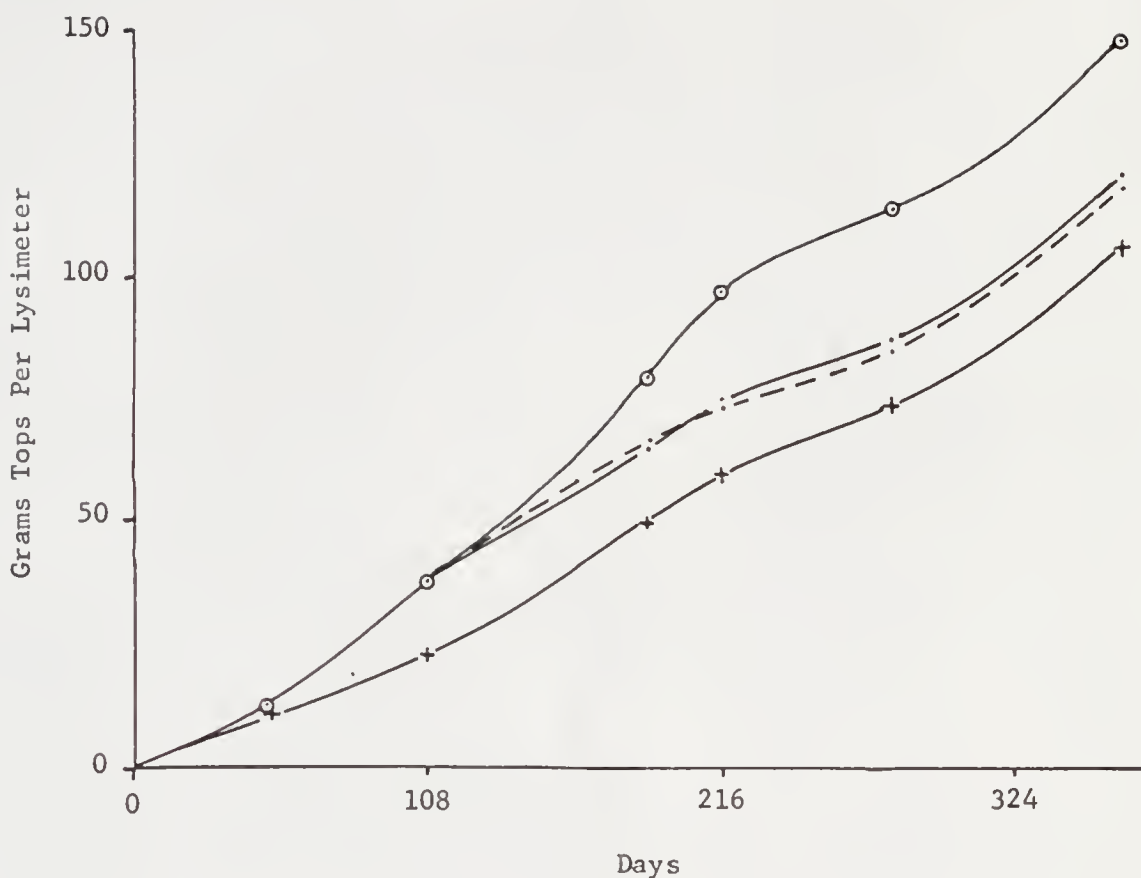
Figure 1--Cumulative dry matter yields of coastal bermudagrass
tops from lysimeters. Averages of three replications.

Treatments Per Lysimeter

·————· $N*H_4NO_3$, 85.6 meq. N

·— — —· NH_4N*O_3, 84.2 meq. N

X————X U-F*, 85.7 meq. N

o————o U-F*, 171.5 meq. N

*Indicates N^{15} labeling.

Table 4--Total N in coastal bermudagrass tops from lysimeters.

N treatment		Meq. N in tops							
	Meq. per	Harvest date (days after fertilization)							
Source	lysimeter	47	51	108	189	216	278	363	Total
N*H₄NO₃	85.6[a]	10.6	28.8	18.2	10.4	7.0	7.3	9.7	92.0
	85.6[a]	9.0	18.3	25.9	11.9	7.5	6.7	13.1	92.4
	85.6[a]	9.4	23.7	26.0	11.9	5.9	6.2	12.5	95.6
Average uptake		9.7	23.6	23.4	11.4	6.8	6.7	11.8	93.4
NH₄N*O₃	84.2[a]	3.9	37.3	19.4	13.0	7.2	7.6	10.6	99.0
	84.2[a]	4.4	22.1	24.0	10.5	7.6	6.6	13.2	88.4
	84.2[a]	6.0	22.8	24.8	11.2	7.0	6.5	12.4	90.7
Average uptake		4.8	27.4	22.7	11.6	7.3	6.9	12.1	92.8
U-F*	85.7[a]	5.9	15.6	13.6	12.5	7.3	9.1	15.5	79.5
	85.7[a]	4.4	18.1	13.3	14.4	7.6	7.4	12.5	77.7
	85.7[a]	9.0	12.2	9.6	11.6	7.4	6.9	10.1	66.8
Average uptake		6.4	15.3	12.2	12.9	7.4	7.8	12.7	74.7
U-F*	171.5[b]	8.4	21.3	22.8	20.4	11.6	9.6	12.2	106.3
	171.5[b]	9.2	21.7	24.0	21.7	14.3	9.6	14.6	115.1
	171.5[b]	7.5	22.4	27.3	29.6	11.8	8.6	13.7	120.9
Average uptake		8.4	21.8	24.7	23.9	12.6	9.3	13.5	114.2

*Indicates N¹⁵ labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.
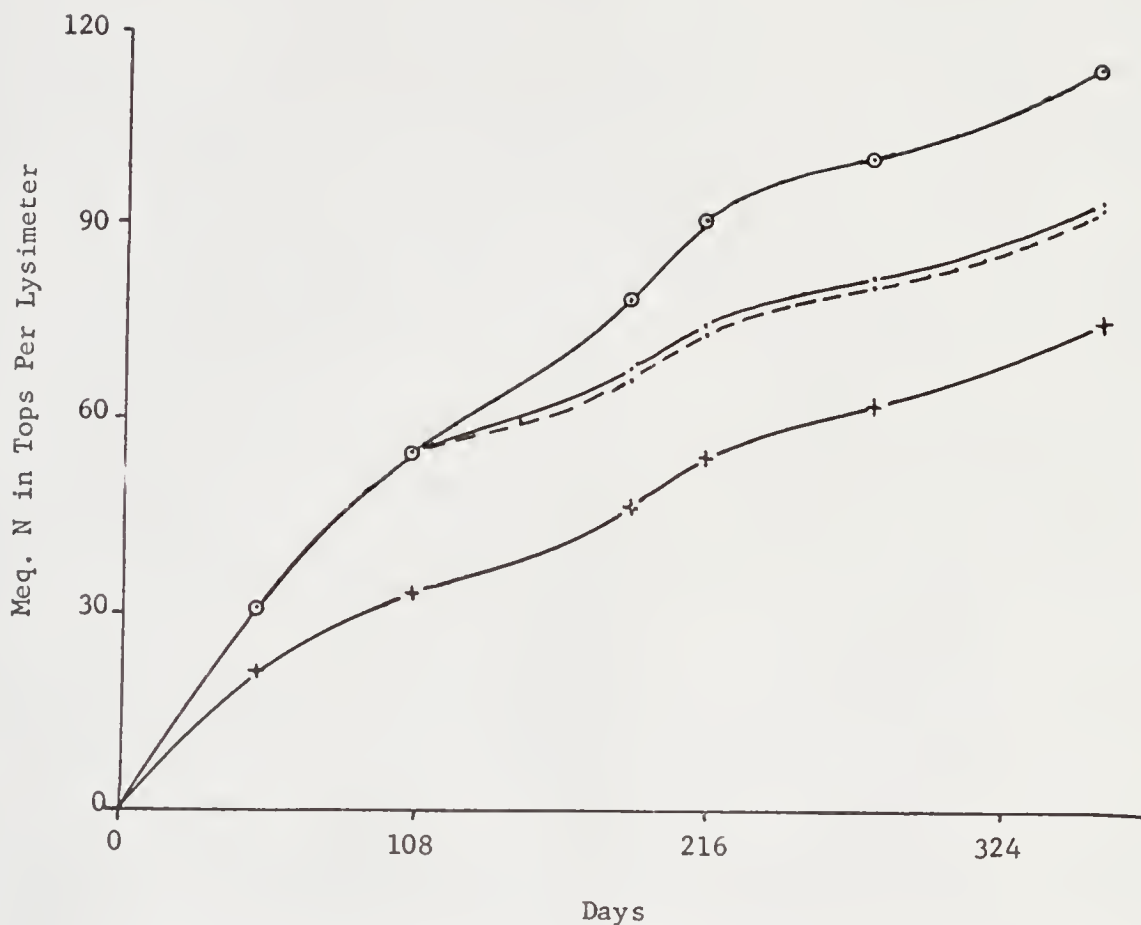
Figure 2--Cumulative total N found in coastal bermudagrass tops from lysimeters.

Treatments Per Lysimeter

·———————· $N*H_4NO_3$, 85.6 meq. N

·— — — —· NH_4N*O_3, 84.2 meq. N

+———————+ U-F*, 85.7 meq. N

⊙———————⊙ U-F*, 171.5 meq. N

*Indicates N^{15} labeling.

matter yields, with one noteworthy exception. The relative differences in N uptake between treatments are much more pronounced than the relative differences in dry matter yields between treatments. This in- dicates that N was more efficient in producing dry matter when it was absorbed in the smaller quantities than when absorbed in the larger quantities. This phenomenon is exemplified by the fact that both ammonium nitrate treatments and the double rate of urea-formaldehyde treatment yielded 1.30 grams of dry matter per meq. N absorbed while the standard rate of urea-formaldehyde treatment yielded 1.43 grams of dry matter per meq. N over the duration of the study.

Comparable dry matter yields and N uptake are noted for ammonium nitrate at the standard rate and urea-formaldehyde at the double rate through the 108-day harvest. Thereafter, the higher rate of urea- formaldehyde produced significantly higher yields of both dry matter and total N. The double rate of urea-formaldehyde and the stardard rate of ammonium nitrate evidently supplied approximately equivalent amounts of readily available N. Continued release of slowly available N from urea-formaldehyde produced increased yields over ammonium nitrate once the readily available N was absorbed or immobilized.

The foregoing data on yields have been presented for each individual harvest date. Yields from these seven individual harvest dates were combined into three composite samples for analysis of N^{15}/N^{14} isotope ratio.

It is important to note that the same amount of total N, but half as much N^{15}-labeled N, was added in the ammonium nitrate treatments as was applied in the standard rate of urea-formaldehyde. This is because the two ammonium nitrate treatments were differentially tagged on either

the ammonium or the nitrate ion. A valid estimate of the behavior of the total N in the ammonium nitrate molecule is obtained by adding the recoveries of the labeled ammonium and labeled nitrate sources together.

The total N and N^{15}-labeled fertilizer N contained in the three harvests are shown in Tables 5 and 6, respectively. These data substantiate the previous statement that approximately the same amount of readily available N was supplied in the standard rate of ammonium nitrate as in the double rate of urea-formaldehyde.

Cumulative total N and N^{15}-labeled fertilizer N uptake data for ammonium nitrate (Figure 3), and for the two rates of urea-formaldehyde (Figure 4), are presented graphically. The proportion of the total N taken up by the bermudagrass from the fertilizer decreased throughout the season. An average of over 71 per cent of the total N taken up during the first 108 days from the ammonium nitrate as well as from the double rate of urea-formaldehyde treatments was labeled fertilizer N. Only 61 per cent of the total N recovered from the standard rate of urea-formaldehyde for the first 180 days was obtained from applied fertilizer (Table 7). Ammonium nitrate and urea-formaldehyde, at the standard rate, contributed comparable quantities of N^{15}-labeled fertilizer N to the grass for the remainder of the year. This indicates that the N availability patterns of comparable rates of these materials differed only for the first 108 days in this study. The relative uptake of labeled urea-formaldehyde N did not increase significantly over an equivalent application rate of ammonium nitrate N in the last harvests.

Table 5--Total N in composited samples of coastal bermudagrass tops from lysimeters.

| N treatment | | Meq. N in tops | | | |
Source	Meq. per lysimeter	0-108 days	109-216 days	217-363 days	Total
$N*H_4NO_3$	85.6[a]	57.5	17.4	17.0	91.9
	85.6[a]	53.2	19.4	19.8	92.4
	85.6[a]	59.1	17.8	18.7	95.6
Average uptake		56.6	18.2	18.5	93.3
NH_4N*O_3	84.2[a]	60.6	20.2	18.2	99.0
	84.2[a]	50.6	18.1	19.8	88.5
	84.2[a]	53.5	18.2	18.9	90.6
Average uptake		54.9	18.8	19.0	92.7
U-F*	85.7[a]	35.1	19.8	24.6	79.5
	85.7[a]	35.8	22.1	19.9	77.8
	85.7[a]	30.7	19.0	17.0	66.7
Average uptake		33.9	20.3	20.5	74.7
U-F*	171.5[b]	52.4	32.0	21.9	106.3
	171.5[b]	54.9	36.0	24.2	115.1
	171.5[b]	57.2	41.4	22.3	120.9
Average uptake		59.8	36.5	22.8	114.1

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.

Table 6--N^{15} labeled fertilizer N recovered in coastal bermudagrass tops from lysimeters.

N treatment		Meq. N^{15}-labeled N recovered			
Source	Meq. per lysimeter	0-108 days	109-216 days	217-363 days	Total
$N^*H_4NO_3$	42.8^a	19.6	2.8	1.7	24.1
	42.8^a	18.0	3.9	2.4	24.3
	42.8^a	20.3	3.5	2.0	25.8
Average recovery		19.3	3.4	2.0	24.7
$NH_4N^*O_3$	42.1^a	23.2	3.8	1.6	28.6
	42.1^a	19.6	3.9	2.5	26.0
	42.1^a	20.5	3.7	2.1	26.3
Average recovery		21.1	3.8	2.1	27.0
U-F*	85.7^a	19.2	7.8	5.6	32.6
	85.7^a	25.8	8.7	4.2	38.7
	85.7^a	17.4	7.7	3.8	28.9
Average recovery		20.8	8.1	4.6	33.5
U-F*	171.5^b	36.8	16.9	7.2	60.9
	171.5^b	38.6	18.0	8.6	65.2
	171.5^b	41.8	23.3	8.1	73.2
Average recovery		39.0	19.4	8.0	66.4

*Indicates N^{15} labeling.

[a]Total application approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.
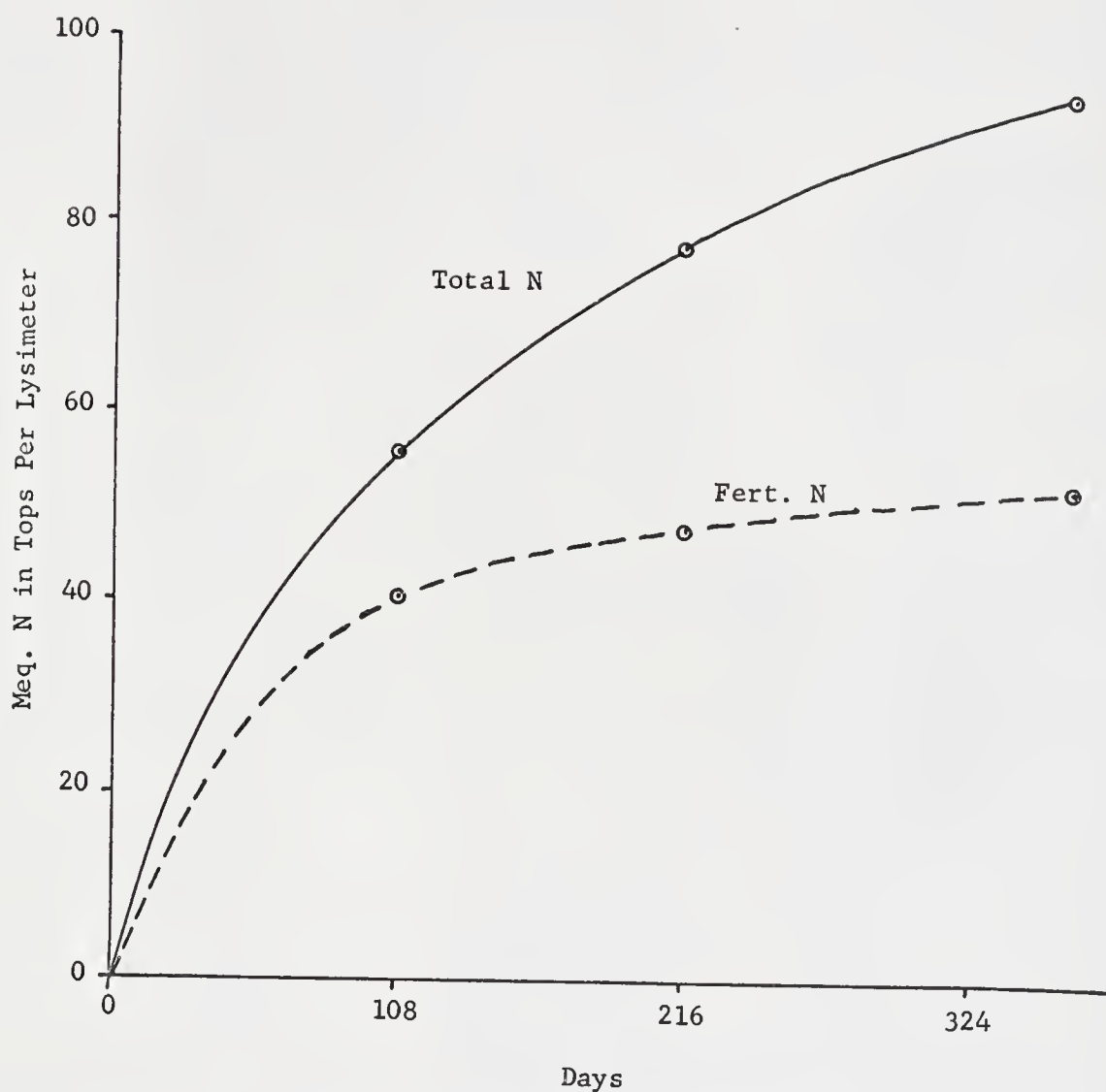
Figure 3--N found in grass tops after application of 85 meq. N as N^{15}-labeled ammonium nitrate. Sum of ammonium and nitrate recoveries.
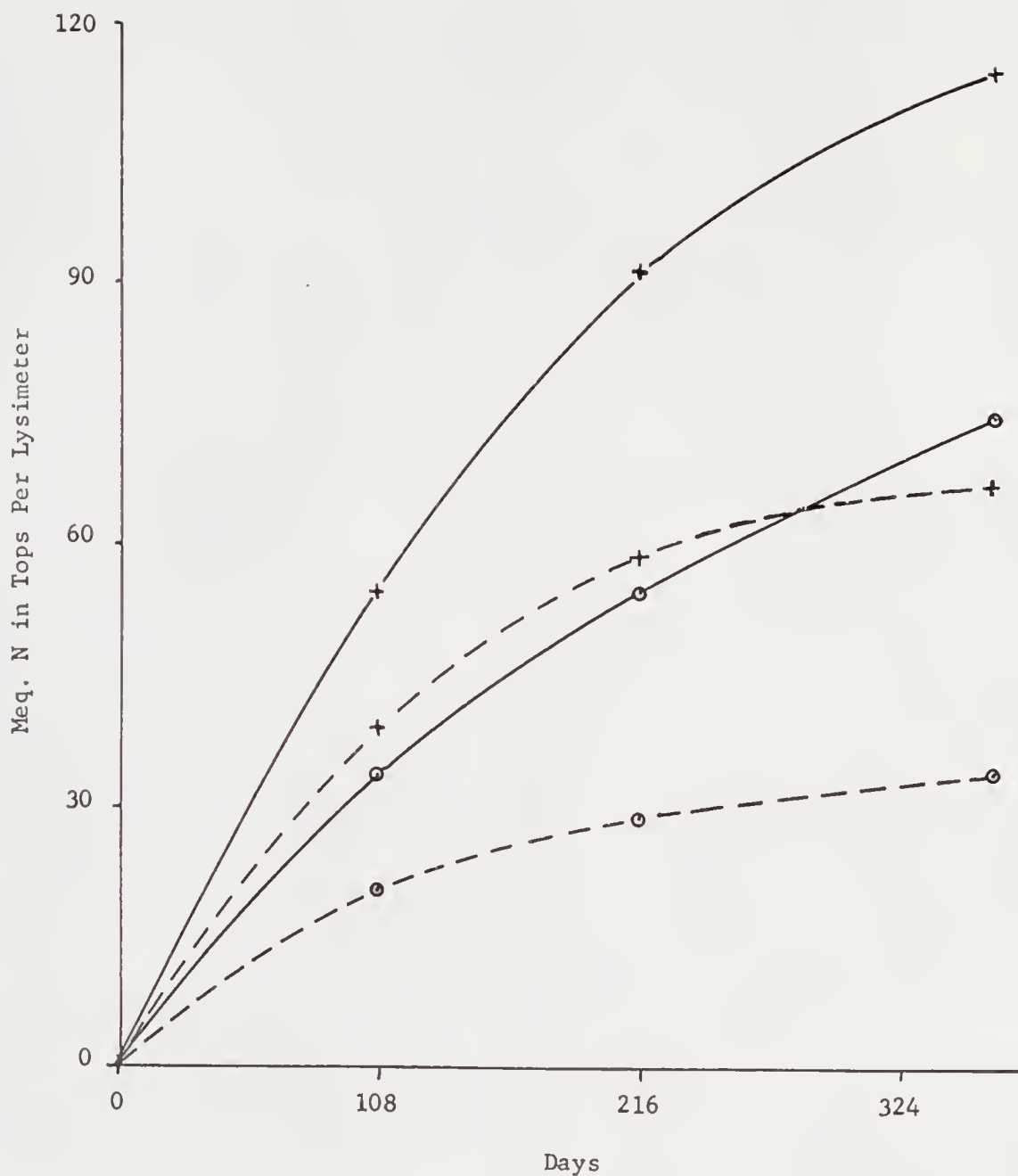
Figure 4--N found in grass tops after application of 85.7 and
171.5 meq. N as N^{15}-labeled urea-formaldehyde.

Legend

+ ——————— +   Total N, 171.5 meq. N rate

+ — — — — + N^{15}-labeled N, 171.5 meq. N rate

◉ ——————— ◉   Total N, 85.7 meq. N rate

◉ — — — — ◉ N^{15}-labeled N, 85.7 meq. N rate

Table 7--Per cent of total N absorbed by coastal bermudagrass in lysimeters which was obtained from N^{15}-labeled fertilizer.

N treatment		Per cent absorbed			
Source	Meq. N* per lysimeter	0-108 days	109-216 days	217-363 days	363 day average
$N*H_4NO_3$	42.8[a]	34.1	15.8	10.0	26.1
	42.8[a]	33.8	20.3	12.3	26.3
	42.8[a]	34.4	19.8	10.5	27.0
Average per cent		34.1	18.6	11.0	26.5
NH_4N*O_3	42.1[a]	38.3	18.5	9.0	28.9
	42.1[a]	38.7	21.7	12.8	29.4
	42.1[a]	38.3	20.4	11.2	29.0
Average per cent		38.4	20.2	11.0	29.1
U-F*	85.7[a]	54.6	39.5	23.0	41.1
	85.7[a]	72.1	39.4	21.0	49.7
	85.7[a]	56.8	45.6	22.7	43.5
Average per cent		61.1	41.5	22.2	44.8
U-F*	171.5[b]	70.2	52.7	33.1	57.3
	171.5[b]	70.4	49.9	35.6	56.7
	171.5[b]	73.0	56.3	36.5	60.6
Average per cent		71.2	53.0	35.1	58.2

*Indicates N^{15} labeling.

[a]Total application approximates 150 pounds N per acre

[b]Approximates 300 pounds N per acre.

The form or amount of N added to the lysimeter soils had no differentially significant* effects on the release of soil N (Table 8), with one exception. During the 109 to 216-day period the double rate of urea-formaldehyde produced a greater absorption of soil N by bermuda-grass than did the other treatments. This indicates that an appreciable exchange of fertilizer N with soil N did not take place during the interval immediately after treatment applications. However, during the 109 to 216-day period the larger amount of fertilizer N remaining in the soils treated with the higher rate of urea-formaldehyde allowed a large exchange between fertilizer and soil N. The larger amounts of fertilizer N in the soil during this period possibly caused greater root growth, resulting in more efficient utilization of both soil and fertilizer N.

The absorption of fertilizer N exceeded the absorption of soil N, only during the first 108-day period for the standard rate of both materials, and for the first and second 108-day periods for the double rate of urea-formaldehyde. An average of 33 meq. of fertilizer N and 41 meq. of soil N was absorbed in one year, after the addition of 85 meq. N (standard rate) as urea-formaldehyde. The total absorption of fer-tilizer N exceeded total absorption of soil N for the other treatments.

In general, soil N can be divided into two broad groups: available mineralized N, and currently unavailable immobilized N. The available N pool in the lysimeter soils is supplied from both the mineralization of unavailable soil N and the mineralization or

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*It should be pointed out that statistical precision is very low for this experimental design, since it contains only four treat-ments, three replications and six degrees of freedom for error. Only gross differences are detectable statistically.

Table 8--Content of soil and fertilizer N in coastal bermudagrass tops grown in lysimeters and fertilized with N^{15}-labeled materials.[a]

N treatment Source	Meq. per lysimeter	1-108 days		109-216 days		217-363 days		Total	
		Fert. N Meq.	Soil N Meq.	Fert. N Meq.	Soil N Meq.	Fert. N Meq.	Soil N Meq.	Fert. N Meq.	Soil N Meq.
NH_4NO_3[b]	84.9	40.4	15.4	7.2	11.3	4.1	14.6	51.7	40.8
U-F	85.7	20.8	13.1	8.1	12.2	4.6	15.9	33.4	41.2
U-F	171.5	39.0	15.8	19.4	17.1	8.0	14.8	66.4	47.6

[a]Averages of three replications.

[b]These values obtained by combining ammonium and nitrate data of Table 6.

solubilizing of fertilizer N. There are two forces competing to immobilize the N once it is in the pool of available N: plant roots and soil micro-organisms.

The pool of available soil N was flooded by the addition of fertilizers which contained large amounts of readily available N. All of the N in the ammonium nitrate sources was readily available, and indications are that approximately half of the N in the urea-formaldehyde source was readily available. Much of the available N was absorbed by the growing bermudagrass while some was incorporated into microbial tissue. The nitrate-N was very vulnerable to leaching at this time, but no excessive rainfall occurred to cause leaching.

By the end of the first 108-day period, the great excess of available N had been immobilized through the two pathways. A steady state condition appears to have been approached in which the available N pool was replenished by mineralization of soil organic N; and, in the case of urea-formaldehyde treatments, by mineralization of the slowly hydrolyzable portions. By this time, the organic soil N had been considerably enriched with N^{15} which had been immobilized from the fertilizer N.

After the first 108-day period the N^{15}-labeled fertilizer N, supplied to the available N pool (as measured by plant uptake), was not appreciably higher where urea-formaldehyde was applied than where ammonium nitrate was applied at an equivalent rate. This indicates that the mineralization of labeled N from the urea-formaldehyde treated soil, plus the hydrolysis of residual urea-formaldehyde, yielded no more labeled N to the available N pool than the mineralization of soil treated with the same rate of labeled ammonium nitrate.

Where a double rate of urea-formaldehyde was applied, the steady state condition appears to have been approached slightly later and produced a higher level of N in the available pool. As N was removed from the available pool by the grass, an increasingly smaller amount of N replenished the pool from mineralization of residual urea-formaldehyde. Since considerable urea-formaldehyde was residual in the soil (see page 52), it appears that this fertilizer material was composed of a group of compounds ranging from readily available to increasingly unavailable compounds.

There have been numerous methods proposed for evaluating the relative efficiencies of various forms of fertilizer N. Methods for mathematically estimating N transformations advanced by Kirkham and Bartholomew (48) have been mentioned in a previous section. Three basic requirements for the validity of their equations are not met by the data presented in this paper. First, there must be no loss of N from the system. Second, the quantity of added N must be very small relative to total N in soil. The soil used in the lysimeter study contained approximately 330 pounds of total N per acre (by Kjeldahl analysis) in the surface 6 inches of soil. The application rates of 150 and 300 pounds N per acre were very substantial amounts compared to this. Third, the rates of mineralization and immobilization must be constant within sampling time intervals. The sampling intervals were much too long to accept this assumption.

Fried and Dean (35) proposed a method for determining the quantity of an available nutrient in a soil using tracer techniques. This method is an adaptation of the commonly used technique for analysis by isotope

dilution. The method estimates the amount of the nutrient in the soil
which has an availability to the plant equal to that of the added
nutrient form, over a given period of time. Fried and Dean's "A" value
may be more appropriately called the equivalent diluent of the soil
nutrient, for the N data presented in this paper. Calculation of this
value is as follows:

$$A = \frac{B(1-y)}{y}$$

where A = equivalent diluent of soil nutrient; B = amount of nutrient
applied; y = proportion of the nutrient in the plant derived from
applied fertilizer.

This principle was applied to the lysimeter recovery data in
Table 7. An equivalent diluent was calculated which represents the
quantity of N from the soil which, if mixed with the entire addition of
tracer N, would have produced the dilution observed in the plant-recovered
N. The standard rate application of ammonium nitrate had equivalent
diluents of 55 pounds of soil N per acre for the first 108 days and
116 pounds for the total 363 days. The standard rate of urea-
formaldehyde had equivalent diluents of 93 and 180 pounds soil N per
acre for the two periods. The double rate of urea-formaldehyde had
equivalent diluent values of 119 and 211 pounds of soil N per acre for
these periods.

The calculations show that the equivalent diluent of soil N in-
creased markedly with time. This indicates a continuous exchange of
tracer N and unavailable soil N throughout the experiment. The lower
equivalent diluent values for ammonium nitrate as compared to the same

rate of urea-formaldehyde shows that there was roughly one and two-thirds times as much N in the soil having availability equal to the urea-formaldehyde N, as there was N in the soil with availability equal to ammonium nitrate N.

Doubling the rate of urea-formaldehyde N increased the equivalent diluent of soil N. This indicates that doubling the rate of N atoms applied caused an increase in exchange with soil N atoms.

It is worthy to note that the equivalent diluent value obtained for ammonium nitrate during the first 108 days (55 pounds N) is roughly half the equivalent diluent value of the average of the two rates of urea-formaldehyde during this period (93 and 119 pounds N). It would appear from these data that approximately half of the N supplied in the double rate of urea-formaldehyde was as available to the grass during the first 108 days as the N supplied in ammonium nitrate.

The quantity of available nutrient in this experiment was not a constant value for a given soil, as was stated by Fried and Dean. The available quantity of soil N, or equivalent diluent, varied with time, application rate and form of N applied.

Absolute values obtained by these calculations may be of little importance because of concentrated fertilizer placement (as opposed to uniform incorporation), loss of N from the system and non-applicability of slowly available urea-formaldehyde to this type of analysis. However, relative values for the various treatments at the different sampling periods are of value.

In general, the higher rate of urea-formaldehyde provided a more desirable N uptake distribution, irrespective of efficiency, than did the standard rate of ammonium nitrate and urea-formaldehyde. As has been

mentioned in a previous section, the urea-formaldehyde material used in this study had a finer particle size, more water soluble N and a higher activity index than standardized commercial materials. This possibly caused the N of the urea-formaldehyde material used in this study to be more readily available than would have been the case had a commercial urea-formaldehyde been used.

Striking differences were obtained between the per cent recovery of N applied as ammonium nitrate and urea-formaldehyde (Table 9 and Figure 5). While approximately 60 per cent of the N applied as ammonium nitrate was recovered in bermudagrass foliage after one year, less than 40 per cent of the urea-formaldehyde N was recovered. The difference in total recoveries between the two materials is due almost entirely to their differential uptake in the first 108-day period.

It appears that approximately two-thirds of the urea-formaldehyde fertilizer N which became available for absorption by bermudagrass in the one-year duration of this study, was in a rapidly available form at application.

No differences in efficiency were noted between the two rates of urea-formaldehyde application. Slight differences were observed between recoveries of ammonium and nitrate ion sources in ammonium nitrate. The largest difference occurred during the first 108-day period, at which time the recovery of nitrate-N was significantly higher than recovery of ammonium-N.

Greater mobility, which resulted in faster absorption of the nitrate-N by bermudagrass roots, possibly accounts for much of the in-creased efficiency of nitrate-N over ammonium-N. Another factor may be the preferential use of ammonium-N by soil micro-organisms. The high

Table 9--Per cent recovery of applied N^{15} in coastal bermudagrass tops from lysimeters.

N treatment		Per cent recovery			
Source	Meq. per lysimeter	0-108 days	109-216 days	217-363 days	Total
$N^*H_4NO_3$	85.6[a]	45.8	6.4	4.0	56.2
	85.6[a]	42.0	9.2	5.7	56.9
	85.6[a]	47.5	8.3	4.6	60.4
Average recovery		45.1	8.0	4.7	57.8
$NH_4N^*O_3$	84.2[a]	55.1	8.9	3.9	67.9
	84.2[a]	46.5	9.4	6.0	61.8
	84.2[a]	48.6	8.8	5.0	62.4
Average recovery		50.0	9.0	5.0	64.0
U-F*	85.7[a]	22.3	9.1	6.6	38.0
	85.7[a]	30.1	10.2	4.9	45.2
	85.7[a]	20.3	9.0	4.5	33.8
Average recovery		24.3	9.4	5.3	39.0
U-F*	171.5[b]	21.4	9.9	4.2	35.5
	171.5[b]	22.5	10.5	5.0	38.0
	171.5[b]	24.4	13.6	4.7	42.7
Average recovery		22.8	11.3	4.7	38.8

Coefficient of variation for total recoveries is 10.1 per cent.

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.
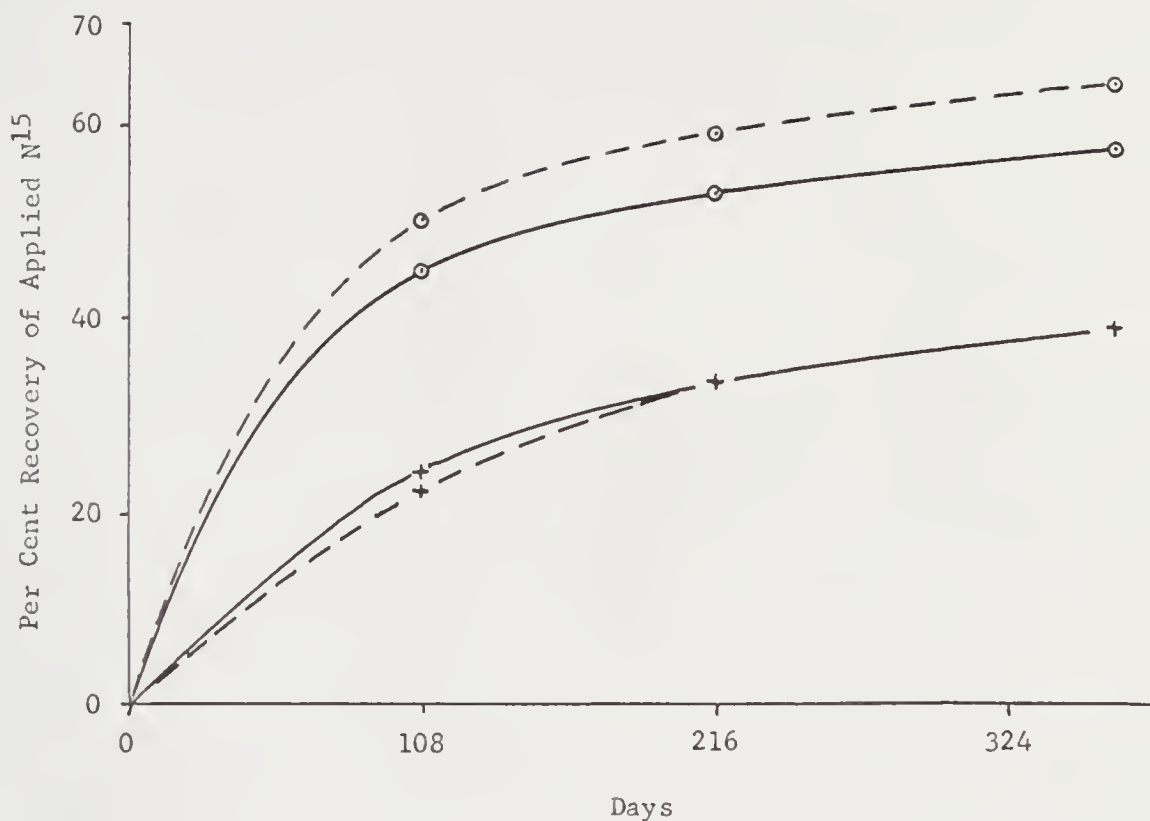
Figure 5--Cumulative per cent recovery of applied N^{15} in coastal bermudagrass tops from lysimeters.

Treatments Per Lysimeter

⊙————⊙ $N*H^+$-N, in NH_4NO_3, 85.6 meq. N

⊙— — —⊙ $N*O_3^-$-N, in NH_4NO_3, 84.2 meq. N

+————+   U-F*, 85.7 meq. N

+— — — —+   U-F*, 171.5 meq. N

*Indicates N^{15} labeling.

recovery of nitrate-N indicates that conditions favorable for bacterial denitrification or leaching did not exist during the early stages of this study.

Root weights and total N recovered in coastal bermudagrass roots showed slight variations with different N treatments (Table 10). The precision of this experiment was not sufficient to show these differences to be statistically significant. Recovery of N^{15}-labeled fertilizer N in the roots appeared to be slightly higher for ammonium nitrate treatments than for urea-formaldehyde treatments.

Soluble plus exchangeable N within the treated soil zones at the termination of the experiment was not affected by N source or rate. Amounts of soluble plus exchangeable N within the cores varied between 6 and 10 parts per million N.

Large amounts of N^{15}-labeled N were found to be residual in the soil at the termination of the experiment (Table 11). Significantly more N^{15} was detected within the original treatment application cores where ammonium nitrate, labeled on the ammonium ion, was applied than when it was labeled on the nitrate ion. This finding helps to substantiate the general assumption of preferential absorption of ammonium-N over nitrate-N by soil micro-organisms. Another explanation might be that ammonium was adsorbed by organic matter complexes or soil colloids. This reduced immediate mobility and also may have affected its availability to the bermudagrass. One or both of these phenomena could effectively decrease the activity of ammonium ions in relation to nitrate ions in the soil solution.

Roughly 17 per cent ($\pm$ 3) of the N^{15} applied as ammonium nitrate was recovered in the top 12 inches of lysimeter soil at the termination

Table 10--Weights and recoveries of N in bermudagrass roots grown in lysimeters and fertilized with N^{15}-labeled materials.

N treatment		Total yield		Recovery of N^{15}	
Source	Meq. per lysimeter	Grams	Meq. N	Meq. Fert. N	Per cent
$N^*H_4NO_3$	85.6[a]	69.0	20.6	2.9	6.7
	85.6[a]	62.8	21.4	3.1	7.3
	85.6[a]	60.8	19.6	2.7	6.3
Averages		64.2	20.5	2.9	6.8
$NH_4N^*O_3$	84.2[a]	66.7	22.4	3.0	7.1
	84.2[a]	48.9	18.2	2.8	6.6
	84.2[a]	54.9	19.9	2.8	6.7
Averages		56.8	20.1	2.9	6.8
U-F*	85.7[a]	49.4	17.2	4.5	5.2
	85.7[a]	41.3	15.9	4.0	4.6
	85.7[a]	50.8	19.7	5.5	6.4
Averages		47.6	17.6	4.6	5.4
U-F*	171.5[b]	67.8	26.5	8.9	5.2
	171.5[b]	67.9	22.4	7.9	4.6
	171.5[b]	59.6	22.5	9.4	5.5
Averages		65.1	23.8	8.8	5.1

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.

Table 11--Content of native soil N and residual N^{15}-labeled fertilizer N in lysimeter soil after one year of cropping with coastal bermudagrass.[a]

N Source	$N*H_4NO_3$	NH_4N*O_3	U-F*	U-F*
N* Rate per lysimeter	42.8 meq. $N*H_4$[b]	42.1 meq. $N*O_3$[b]	85.7 meq. N*[b]	171.5 meq. N*[c]
Fertilized Cores:				
Grams soil	2800	2800	2800	2800
Total N, meq.	70.0	72.2	88.01	93.99
Residual N^{15}, meq.	2.1	1.2	20.9	32.1
0-7 Inches Between Cores:				
Grams soil	12900	12700	12800	13000
Total N, meq.	320.3	339.8	332.1	339.7
Residual N^{15}, meq.	4.4	3.8	7.4	16.8
7-12 Inch Zone:				
Grams soil	12900	12800	12400	13100
Total N, meq.	455.7	460.4	457.3	454.9
Residual N^{15}, meq.	1.5	1.6	2.7	4.0
12-36 Inch Zone:				
Grams soil	55500	55800	56600	56000
Total N, meq.	577	625	547	622
Residual N^{15}, meq.	--	--	--	--

Coefficient of variation for residual fert. N* is 10.1 per cent.

*Indicates N^{15} labeling.

[a]Averages of three replications.

[b]Total application approximates 150 pounds N per acre.

[c]Approximates 300 pounds N per acre.

of the experiment. This represents the amount of labeled ammonium nitrate-N which was immobilized by soil micro-organisms and not sub- sequently mineralized and adsorbed by the plant, or otherwise lost from the soil. It serves as a measure of the extent of dilution to which soluble fertilizer N was subjected.

Approximately 36 and 31 per cent ($\pm$ 2) of the N^{15} applied as urea-formaldehyde at the standard and double rates, respectively, were found in the surface 12 inches of soil. The per cent of N^{15}-labeled N, re- covered from the soil outside the zones of treatment application, did not vary with treatment. The major portion of N^{15}-labeled urea-formalde- hyde N remained in the zones of application. Whereas 3 to 5 per cent of the N^{15}-labeled ammonium nitrate N was found in the zones of application, 17 to 26 per cent of the labeled urea-formaldehyde N was still in these zones. Assuming that 3 to 5 per cent of the applied urea-formaldehyde N has been immobilized by soil micro-organisms (an assumption has already been made for ammonium nitrate N), roughly 12 to 22 per cent of the applied urea-formaldehyde remained unchanged in the zones of application.

Approximately 24 and 19 per cent ($\pm$ 2) of the urea-formaldehyde N applied at rates of 150 and 300 pounds N per acre, respectively, were found in the zones of application. This was a significantly higher recovery of applied N from the small application rate.

Since treatments were concentrated into 20 per cent of the surface 6 inches of soil, the per acre application rates of N must be multiplied by 5 to give the concentrations of N within the zones of application. The standard application rate amounts to 750 pounds and the double rate amounts to 1,500 pounds of N per acre within the zones of application.

Little is known about the behavior of urea-formaldehyde materials in soils at these concentrations. Perhaps a condition was developed which caused N to be lost as a gas from such a system.

Recoveries of N^{15}-labeled fertilizer N are not shown for the 12 to 36-inch soil zone. Total N values obtained for this zone were quite variable and the amount of N^{15} was not significantly above the normal isotope abundance of N^{15}. Therefore, it is believed that omission of this zone in calculating the total recovery of N^{15}-labeled fertilizer N did not introduce appreciable errors.

Total recoveries of N^{15}-labeled fertilizer materials ranged from 73 to 90 per cent for the 12 lysimeters. Total per cent recoveries for the four N treatments are summarized in Table 12.

Total recoveries of N^{15}-labeled ammonium, nitrate and urea-formaldehyde N at the standard rate showed no significant differences. The double rate of urea-formaldehyde produced a significantly lower recovery of N^{15} than did the standard rate. This difference is accounted-for in the lower recovery of residual urea-formaldehyde N from the double rate in the zones of application.

Regardless of the source applied, a considerable amount of N was unaccounted-for. Many possibilities exist which might contribute to this discrepancy. Among the most plausible are insects, animals, denitrification of soil and leachate N, unmeasurable N^{15} in the 12 to 36-inch zone, chemical decomposition and volatilization, and experimental error.

A discussion of experimental error is important. The primary sources of error in this experiment in their order of relative magnitude were: 1) variation between replicate lysimeters; 2) subsample variation;

Table 12--Per cent recovery of N^{15}-labeled ammonium nitrate and urea-formaldehyde from lysimeters cropped with coastal bermudagrass for one year.[a]

N treatment		Plant tops				Plant	Soil				Total
Source	Meq. N* per lysimeter	0-108 days	109-216 days	216-363 days	Total	roots	0-6 inch cores	Between cores	7-12 inch zone	Total	recovery
		%	%	%	%	%	%	%	%	%	%
NH_4NO_3:											
N*H$_4$-N	42.80[b]	45.1	8.0	4.8	57.9	6.8	4.9	10.3	3.6	18.8	83.5
N*O$_3$-N	42.12[b]	50.0	9.0	5.0	64.0	6.8	2.8	9.1	3.7	15.6	86.4
U*-F	85.75[b]	24.3	9.4	5.3	39.0	5.4	24.3	8.7	3.1	36.1	80.5
U-F	171.50[c]	22.8	11.3	4.6	38.7	5.1	18.7	9.8	2.4	30.9	74.7

Coefficient of variation for total recovery is 4.2 per cent.

*Indicates N^{15}-labeling.

[a] Averages of three replications.

[b] Total application approximates 150 pounds N per acre.

[c] Approximates 300 pounds N per acre.

3) analytical errors in total N determinations; 4) determination of N^{15} tracer content.

Errors in determining N^{15} content of N samples were less than 0.6 per cent of the mean values obtained. Errors in the determination of total N (discrepancies between duplicate subsamples) were approximately 1 per cent of the mean values for plant materials and 2 per cent of the mean values for soil samples.

A large source of error existed in obtaining representative soil samples from individual lysimeters. An estimation of the magnitude of this error is not possible from the data.

The largest source of error was the variation between replicate lysimeters. While this error is not separated from analytical errors in this study, its magnitude is many times larger. This is exemplified in the coefficient of variation (standard deviation as a per cent of the mean) values of the following yield and recovery data: dry matter yield, 11.9 per cent; per cent recovery of N^{15} in plant tops, 10.1 per cent; per cent recovery of N^{15} in soils, 10.1 per cent; and per cent total recovery of N^{15}, 4.2 per cent.

Greenhouse Phase

This study differed from the lysimeter study in certain important categories: first, essentially three soils were used; second, a control treatment, with no N application was included; third, only one rate of urea-formaldehyde was included. The double rate of 300 pounds N per acre was used because it was anticipated that it would supply approximately as much readily available N as the 150 pounds N per acre from ammonium

nitrate; fourth, the N applications were incorporated uniformly in the surface 4 inches of soil in each pot (in the lysimeter study, applications were concentrated in cores which comprised 20 per cent of the surface 6 inches of soil); fifth, the data for the greenhouse study are much more uniform than those from the lysimeter study. This could be due to more uniform temperatures and watering, closer control of insects, animals and wind currents and a more restricted soil volume.

Yields and recovery of labeled fertilizer N in foliage (Table 13), roots (Table 14) and soils (Table 15) are presented in tabular form.

No significant differences were noted in yields or per cent N recovery due to soil type or pH of Leon fine sand. However, it is evident that the Ona soil contained more organic matter than the Leon, since it contains more soil N. This increased amount of organic matter appears to have caused more nitrate-N to be immobilized from ammonium nitrate in this soil than in Leon fine sand.

With the above exception, the soils used behaved similarly in all respects throughout the study. For this reason, averages for the three soils will be used to discuss the N treatments.

The absorption of labeled ammonium-N into plant tops from ammonium nitrate was significantly lower than the absorption of nitrate-N from ammonium nitrate. This phenomenon was observed in the lysimeter study, but not to so great an extent.

Combining the recoveries of labeled ammonium and nitrate-N shows that an average of approximately 64 per cent of the N applied as ammonium nitrate was found in the plant tops. This compares with about 55 per cent recovery of urea-formaldehyde N supplied at twice the rate. These recoveries of N are considerably higher than those obtained in the

Table 13--Yields and recovery of labeled fertilizer N in tops of coastal bermudagrass and millet grown in greenhouse pots.

| Soil | | N applied | | Tops yield | | | % Recovery of applied N* |
Type	Final pH	Source	Meq.	Grams	Meq. N	Meq. Fert. N*	
Leon fine sand pH = 6.6	7.1	None	0	16.4	14.2	--	--
	6.6	N*H$_4$NO$_3$	39.5^a	33.9	42.5	18.9	69.8
	6.6	NH$_4$N*O$_3$	39.9^a	38.8	45.2	15.9	79.9
	6.4	U-F*	81.7^b	46.0	61.3	46.1	56.4
Leon fine sand pH = 5.5	6.0	None	0	17.6	15.8	--	--
	5.7	N*H$_4$NO$_3$	39.5^a	34.0	45.2	14.2	71.8
	5.7	NH$_4$N*O$_3$	39.9^a	33.8	47.1	15.6	78.1
	5.6	U-F*	81.7^b	45.6	64.8	46.7	57.2
Ona fine sand pH = 5.6	5.8	None	0	20.3	17.8	--	--
	5.6	N*H$_4$NO$_3$	39.5^a	36.9	45.6	13.4	67.7
	5.6	NH$_4$N*O$_3$	39.9^a	36.6	46.5	14.7	73.9
	5.6	U-F*	81.7^b	47.0	63.6	42.4	51.8
Average of three soils	--	None	0	18.1	15.9	--	--
	--	N*H$_4$NO$_3$	39.5^a	34.9	44.4	13.8	69.8
	--	NH$_4$N*O$_3$	39.9^a	34.7	46.3	15.4	77.3
	--	U-F*	81.7^b	46.2	63.2	45.1	55.2

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.

Table 14--Yields and recovery of labeled fertilizer N in roots of coastal bermudagrass grown in greenhouse pots.

Soil		N applied		Root yield			% Recovery of
Type	Final pH	Source	Meq.	Grams	Meq. N	Meq. Fert. N*	applied N*
Leon fine	7.1	None	0	2.5	0.7	--	--
sand	6.6	$N*H_4NO_3$	39.5^a	4.1	1.7	0.4	2.3
pH = 6.6	6.6	NH_4N*O_3	39.9^a	4.3	1.9	0.5	2.5
	6.4	U-F*	81.7^b	5.7	3.6	2.4	3.0
Leon fine	6.0	None	0	2.6	0.8	--	--
sand	5.7	$N*H_4NO_3$	39.5^a	4.2	1.9	0.5	2.6
pH = 5.5	5.7	NH_4N*O_3	39.9^a	3.8	1.9	0.5	2.3
	5.6	U-F*	81.7^b	4.8	3.1	2.0	2.5
Ona fine	5.8	None	0	3.1	1.1	--	--
sand	5.6	$N*H_4NO_3$	39.5^a	5.4	2.6	0.6	3.2
pH = 5.6	5.6	NH_4N*O_3	39.9^a	5.4	3.2	0.8	4.1
	5.6	U-F*	81.7^b	6.8	5.0	3.0	3.6
Average of	---	None	0	2.7	0.8	--	--
three soils	---	$N*H_4NO_3$	39.5^a	4.6	2.1	0.5	2.7
	---	NH_4N*O_3	39.9^a	4.4	2.3	0.6	3.0
		U-F*	81.7^b	5.8	3.9	2.5	3.0

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.

Table 15--Recovery of labeled fertilizer N in soils of greenhouse pots cropped with coastal bermudagrass and millet.

| Soil | | N applied | | | Soil Analysis | | |
Type	Final pH	Source	Meq.	Grams soil	Meq. total N	Meq. Fert. N*	% Recovery of applied N*
Leon fine sand pH = 6.6	7.1	None	0	9600	--	--	--
	6.6	N*H$_4$NO$_3$	39.5^a		164.8	3.04	15.4
	6.6	NH$_4$N*O$_3$	39.5^a		177.6	1.58	7.9
	6.4	U-F*	81.7^b		189.8	24.48	30.0
Leon fine sand pH = 5.5	6.0	None	0		--	--	--
	5.7	N*H$_4$NO$_3$	39.5^a		212.8	3.47	17.6
	5.7	NH$_4$N*O$_3$	39.9^a		198.1	1.55	7.8
	5.6	U-F*	81.7^b		260.2	27.38	33.5
Ona fine sand pH = 5.6	5.8	None	0		--	--	--
	5.6	N*H$_4$NO$_3$	39.5^a		279.4	3.37	17.1
	5.6	NH$_4$N*O$_3$	39.9^a		302.4	2.63	16.5
	5.6	U-F*	81.7^b		280.0	26.95	33.0
Average of three soils	--	None	0		--	--	--
	--	N*H$_4$NO$_3$	39.5^a		219.0	3.29	16.7
	--	NH$_4$N*O$_3$	39.9^a		226.0	1.92	9.1
	--	U-F*	81.5^b		243.3	26.27	32.2

*Indicates N^{15} labeling.

^{a}Approximates 150 pounds N per acre.

^{b}Approximates 300 pounds N per acre.

lysimeter study. Root yield and recovery data show no differences among N sources.

Soil recoveries of labeled fertilizer N are complimentary to the recoveries of labeled N in plant tops in producing nearly identical total recoveries of the three tagged materials (Table 16). This phenomenon was evident in lysimeter data, but it was not nearly so striking. Total recoveries of labeled fertilizer N, averaged for three soils and three replications, were between 89 and 90 per cent for all three N sources. Individual pot recoveries ranged from 81 to 97 per cent of the N^{15} applied.

The portion of labeled N unaccounted for in the greenhouse pots was not affected by source of N, and was smaller in magnitude than that obtained in the lysimeters. The fact that treatments were applied uniformly throughout the total surface 4 inches of soil in the pots, and not concentrated into cores as in the lysimeters, may help to explain this. It is generally accepted that losses of N from soils increase with increased concentration of N.

A fairly consistent amount of N was unaccounted for from ammonium, nitrate and urea-formaldehyde N treatments in the lysimeter study and in the greenhouse study. This suggests that the loss (assumed to be volatile) occurred after the applied N had entered the biological cycle of soil N. It was not lost directly from the form in which it was applied, except possibly with the high rate of urea-formaldehyde concentrated into small application zones in the lysimeter study.

The inclusion of a control (no N) treatment in the greenhouse pot study enables a comparison to be made between the two methods for

Table 16--Total recovery of labeled fertilizer N from greenhouse pots cropped with coastal bermudagrass and millet.

Soil		N applied		% Recovery of N^{15}-labeled fertilizer N			
Type	Final pH	Source	Meq.	Tops	Roots	Soil	Total
Leon fine sand pH = 6.6	7.1	None	0	--	--	--	--
	6.6	$N*H_4NO_3$	39.5[a]	69.8	2.3	15.4	87.5
	6.6	NH_4N*O_3	39.5[a]	79.9	2.5	7.9	90.3
	6.4	U-F*	81.7[b]	56.4	3.0	30.0	89.4
Leon fine sand pH = 5.5	6.0	None	0	--	--	--	--
	5.7	$N*H_4NO_3$	39.5[a]	71.8	2.6	17.6	92.0
	5.7	NH_4N*O_3	39.9[a]	78.1	2.3	7.8	88.2
	5.6	U-F*	81.7[b]	57.2	2.5	33.5	93.2
Ona fine sand pH = 5.6	5.8	None	0	--	--	--	--
	5.6	$N*H_4NO_3$	39.5[a]	67.7	3.2	17.1	88.0
	5.6	NH_4N*O_3	39.9[a]	73.9	4.1	11.5	89.5
	5.6	U-F*	81.7[b]	51.8	3.6	33.0	88.4
Average of three soils	--	None	0	--	--	--	--
	--	$N*H_4NO_3$	39.5[a]	69.8	2.7	16.7	89.2
	--	NH_4N*O_3	39.9[a]	77.3	3.0	9.1	89.4
	--	U-F*	81.5[b]	55.2	3.0	32.2	90.4

*Indicates N^{15} labeling.

[a]Approximates 150 pounds N per acre.

[b]Approximates 300 pounds N per acre.

calculating recovery of applied N. Data obtained by both methods are presented in Table 17. The ammonium nitrate treatments have been omitted because their recovery data are for either ammonium or nitrate-N and not for the total N.

It appears that the method involving subtraction of a check over-estimates the actual amount of fertilizer N absorbed by plants. However, this method gives a practical evaluation of fertilizer response because it includes the soil N plus fertilizer N taken up by a crop. This method does not involve concern for the immobilization-mineralization relationship in a soil after fertilizer N application. Accuracy with this method would be highest if a soil was cropped until the rate of N uptake was the same from the treated plots as from the checks. The N^{15} method is obviously more precise and better suited for N balance and N loss studies, but it is more laborious, costly and requires a higher degree of technical skill.

Laboratory Phase

Experiment Number 1, in which air was passed over N treated soils, produced no positive results. No measurable amounts of NH_3, NO or NO_2 could be detected in the trapping solutions. It was concluded from this experiment that no significant amounts of N would be volatilized as NH_3, NO or NO_2 from this soil system under aerobic conditions.

The two anerobic experiments, in which N treated soils were incubated in a He atmosphere, provided some interesting results. Data from the second experiment are presented in Table 18. Measurable amounts of

Table 17--Comparison of calculated recoveries of applied urea-formaldehyde N in greenhouse pots by two methods: deduction of checks versus use of N^{15} labeling.

| Soil | | N treatment | | Per cent recovered in | | | |
| | | | | Tops | | Roots | |
Type	Final pH	Source	Meq.	-Check method	N^{15} method	-Check method	N^{15} method
Leon fine sand	6.4	U-F	81.7	57.7	56.4	3.5	3.0
Leon fine sand	5.6	U-F	81.7	60.0	57.2	2.9	2.5
Ona fine sand	5.6	U-F	81.7	56.1	51.8	4.8	3.6
Soils Average	---	U-F	81.7	57.9	55.2	3.7	3.0

Table 18--Qualitative estimation of certain volatile N products formed
during anerobic incubation of three fertilizer materials
in moist soil.

| N treatment | | | Days of incubation | | | | | |
Source	ppm. N	Gas	1	2	3	4	5	6
None	0	N_2	-	-	-	-	-	-
		N_2O	-	-	-	-	-	-
		NO	-	-	-	-	-	-
NH_4NO_3	150	N_2	-	-	+	++	++	++
		N_2O	-	+	+	-	-	-
		NO	-	-	-	-	-	-
U-F	150	N_2	-	-	+	++	++	++
		N_2O	-	-	-	-	-	-
		NO	-	-	-	-	-	-
Urea	150	N_2	-	-	-	-	-	-
		N_2O	-	-	-	-	-	-
		NO	-	-	-	-	-	-

volatile N compounds were formed under anerobic conditions from ammonium nitrate and urea-formaldehyde.

The volatile products and their sequence of formation from the ammonium-nitrate-treated soil were as expected (15,29). The N_2 produced in the urea-formaldehyde-treated soil was surprising. Since no N_2 was produced from the urea-treated soil, it was assumed that the hydrolysis of the two materials proceeded along different pathways.

After this qualitative study, a third experiment was set up to quantitatively measure the products formed from soils anerobically incubated with urea, uramite* and certain similar compounds. Washed uramite was included to determine whether the N_2 was coming from the soluble or the insoluble portion of the uramite. Methylenediurea was included because it is believed to be a principal constituent of the soluble portion of urea-formaldehyde. Hydroxylamine was included to determine if it acted as an intermediate in the oxidation of urea-formaldehyde N to molecular N_2.

The results of this experiment are presented in Table 19. These data substantiate the fact that the N_2 was evolved from the water-soluble non-urea portion of urea-formaldehyde, and that hydroxylamine probably was not an intermediate in this oxidation. It has been reported (32,33) that hydroxylamine is oxidized by soil micro-organisms quantitatively to nitrite. Possibly, nitrite was formed from hydroxylamine, then reduced to N_2 by denitrifying bacteria in the incubation flasks. The extra step of oxidizing to nitrite could cause the observed delay in N_2 production.

*Uramite is a commercial urea-formaldehyde fertilizer material produced by Dupont.

Table 19--N_2 gas production from various N materials incubated anerobically with moist soil at 30°C.

| N treatment | | Repli-cation | Mgm. N_2 in flask with days of incubation | | | | | |
Source	Mgm. N		1	2	3	4	5	6
None	0	1	1.8	1.9	2.1	1.8	2.1	2.0
		2	1.9	1.9	2.0	2.1	2.2	2.2
Uramite, U-F	75[a]	1	3.5	4.3	4.9	6.7	8.0	8.4
		2	3.6	3.7	3.8	4.6	4.6	4.0
Uramite, U-F washed	75[a]	1	1.9	2.0	1.9	2.0	2.1	2.2
		2	1.8	2.0	2.1	1.8	2.0	2.2
Methylene-diurea	75[a]	1	2.5	4.4	5.5	7.7	7.5	8.3
		2	2.8	5.0	6.7	7.8	8.0	7.3
Hydroxylamine	75[a]	1	1.9	2.0	2.0	3.6	4.2	10.9
		2	2.0	2.2	2.2	---	---	---
Urea	75[a]	1	1.9	2.0	2.1	2.1	2.1	2.2
		2	2.1	2.0	1.8	2.1	2.1	1.9

[a]Equivalent to 150 ppm. N.

Volatilization of N from soils treated with urea-formaldehyde and ammonium nitrate under the conditions described above may or may not have been a factor in losses of N from lysimeter and greenhouse soils. While the soil was assumed to be aerobic, it is possible that micro-areas of anerobic conditions were present in water films within soil granules. Very small losses at any one time from such micro-areas might amount to substantial losses of N with extended time.

SUMMARY AND CONCLUSIONS

A study was initiated in October of 1962 to quantitatively deter-
mine the destiny of N applied as urea-formaldehyde and ammonium nitrate
fertilizers. Fertilizer materials were labeled with an excess of N^{15},
and results were based on plant, soil and leachate recovery of labeled N.

The study was carried out in three phases: 1) an outdoor
lysimeter; 2) a greenhouse; 3) a laboratory phase. Primary N recovery
data were obtained from the lysimeter and greenhouse phases. The labora-
tory incubation phase was included as a supplemental portion of this study
to determine the nature of volatile N products which may be formed under
certain conditions from urea-formaldehyde and ammonium nitrate incor-
porated in soil.

The physical set-up of the lysimeter phase consisted of 12 buried
lysimeters 12 inches in diameter and 36 inches deep. The bottoms were
tapped by plastic tubing through which leachate water was removed.
Arrodondo fine sand soil filled the lysimeters in three profile horizon
layers. Coastal bermudagrass was the test crop for the 12-month duration
of the study.

Grass was harvested periodically, yield data was taken and measure-
ments were made on content of total N and N^{15}-labeled fertilizer N. At
the termination of the study, roots were weighed and analyzed, and soils
were analyzed for content of soluble plus exchangeable N, total N and
N^{15}-labeled fertilizer N. Leachates were collected throughout the study
and analyzed for soluble N and N^{15} content.

Treatments used in the lysimeter study were as follows:

1) NH_4NO_3, approximating 150 pounds N per acre, labeled on ammonium-N.

2) NH_4NO_3, approximating 150 pounds N per acre, labeled on nitrate-N.

3) Urea-formaldehyde, approximating 150 pounds N per acre, labeled.

4) Urea-formaldehyde, approximating 300 pounds N per acre, labeled.

The greenhouse phase was conducted in 2-gallon glazed porcelain pots and lasted for eight months. Two soils, one at 2 pH levels, were used. Test crops were coastal bermudagrass for the first seven months and millet for the last month.

Treatments used in the greenhouse study were as follows:

1) No N added.

2) NH_4NO_3, approximating 150 pounds N per acre, labeled on ammonium-N.

3) NH_4NO_3, approximating 150 pounds N per acre, labeled on nitrate-N.

4) Urea-formaldehyde, approximating 300 pounds N per acre, labeled.

Three separate incubation studies were conducted in the laboratory phase. The first was in aerobic and the second and third in anerobic systems. The soil used in all cases was similar to the lysimeter surface soil.

The first incubation experiment involved chemical trapping of NH_3 and acid oxides of N (NO, NO_2). Treatments approximating those of the

lysimeter phase were incorporated into small portions of soil. An air stream passed over the soil and through the trapping solutions.

The second and third incubation experiments consisted of soils ammended with ammonium nitrate, whole urea-formaldehyde, washed urea-formaldehyde, methylenediurea, hydroxylamine and urea in 100 per cent He atmosphere. Qualitative and quantitative measurement was made by gas chromatography of gaseous N products produced in the incubation flasks.

The results obtained from the foregoing experiments serve as bases for the following conclusions.

1) Leaching was not a significant factor in contributing to losses of N under the conditions of this study.

2) Ammonium nitrate produced higher yields of dry matter and total N than the same rate of urea-formaldehyde only during the 52 to 108-day interval. Comparable yields were obtained for the remainder of the study.

3) The double rate of urea-formaldehyde produced the same yields of dry matter and total N as the standard rate of ammonium nitrate for the first 108 days and increased yields thereafter.

4) Approximately half of the N supplied in the urea-formaldehyde material used in this study was as rapidly available as that in ammonium nitrate.

5) Roughly 16 per cent of the N supplied by ammonium nitrate and urea-formaldehyde was residual in the surface 12 inches of soil, presumably immobilized in microbial tissue.

6) Roughly 16 per cent of the N supplied in the urea-formaldehyde material used in this study was apparently unchanged in the zones of application.

7) There was evidence of preferential absorption of ammonium-N over nitrate-N by soil micro-organisms which produced lower recoveries of ammonium-labeled N in the plants and higher recoveries in the soil, while total recovery was unaffected.

8) Roughly 44 and 58 per cent of the N applied as urea-formaldehyde in the lysimeter and greenhouse studies, respectively, were absorbed by the plants.

9) Roughly 68 and 76 per cent of the N applied as ammonium nitrate in the lysimeter and greenhouse studies, respectively, were absorbed by the plants.

10) Regardless of the source, a fairly constant percentage of applied N was unaccounted-for.

11) Increasing the rate of urea-formaldehyde N application in restricted soil zones resulted in an increased loss of N.

12) Factors which might account for the discrepancies in recovery of N are insects, animals, denitrification of soil and leachate N, chemical decomposition and volatilization and experimental errors.

13) The largest source of error was natural variation between replicated treatments. This variation was not excessive. A coefficient of variation value of 4.2 per cent was obtained for the per cent total recovery of applied N.

14) Unaccounted-for N is believed to have been lost as a gas after it entered the organic N complex of the soil, possibly through gradual denitrification in anerobic micro-areas in soil.

15) Decomposition of high concentrations of the soluble portion of urea-formaldehyde in the soil to N_2 gas under anerobic conditions may limit efficiency of this material.

16) Urea does not oxidize anerobically to N_2 as does some fraction of urea-formaldehyde.

17) Apparently hydroxylamine is not an intermediate in the anerobic oxidation of soluble urea-formaldehyde to N_2 gas.

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BIOGRAPHY

Max Arnold Brown was born in Cedar Rapids, Iowa, January 5, 1938.
He graduated from Mechanicsville Community High School, Mechanicsville,
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In June, 1960, the writer was married to Sally Aline Ahrens. They
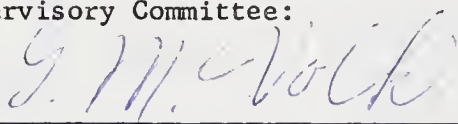have one daughter, Valerie Anne.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Agriculture and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.
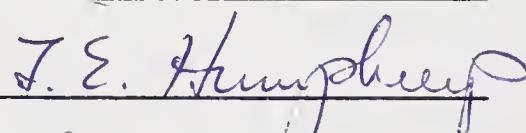
August 8, 1964

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Dean, College of Agriculture

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